

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
10 April 2003 (10.04.2003)

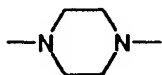
PCT

(10) International Publication Number  
**WO 03/029359 A1**

- (51) International Patent Classification<sup>7</sup>: C09B 62/04, 62/085, 44/16, A61K 7/13
- (21) International Application Number: PCT/EP02/10404
- (22) International Filing Date:  
17 September 2002 (17.09.2002)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
2001 1755/01 24 September 2001 (24.09.2001) CH
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- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:  
— with international search report  
— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 03/029359 A1

(54) Title: CATIONIC REACTIVE DYES



(57) Abstract: Cationic reactive dyes of the general formula  $[A-(D_m-B)_x]^{n+} An^{n-}$  (1), wherein A is the radical of a cationic chromophore selected from the group of the acridine, anthraquinone, azine, azo, azomethine, benzimidazole, cyanine, diazo, dioxazine, ketoimine, methine, monoazo, nitro, oxazine, polymethine, quinoline, thiazole, triarylmethane and xanthene series, D is -NR-, -(NR'-(C<sub>1</sub>-C<sub>7</sub>alkylene)-NR"-), or a piperazinylene of formula (I), wherein R is hydrogen, C<sub>1</sub>-C<sub>4</sub>alkyl, -CO-C<sub>1</sub>-C<sub>4</sub>alkyl, -CO-phenyl, ortho-, meta- or para-(C<sub>6</sub>H<sub>4</sub>)-(C<sub>1</sub>-C<sub>4</sub>alkyl), ortho-, meta- or para-(C<sub>6</sub>H<sub>4</sub>)-(C<sub>1</sub>-C<sub>4</sub>alkylene)-\*N(R<sub>7</sub>R<sub>8</sub>R<sub>9</sub>) or -(C<sub>1</sub>-C<sub>4</sub>alkyl)-\*N(R<sub>7</sub>R<sub>8</sub>R<sub>9</sub>), wherein R<sub>7</sub>, R<sub>8</sub> and R<sub>9</sub> are each independently of the others hydrogen or C<sub>1</sub>-C<sub>4</sub>alkyl, and R' and R" are each independently of the other hydrogen or C<sub>1</sub>-C<sub>4</sub>alkyl, m is an integer 0 or 1, and x is an integer from 1 to 8, n<sup>+</sup> is the charge of the radical  $[A-(D_m-B)_x]$  and is an integer from +1 to +6, n<sup>-</sup> is the charge of the anion and is an integer from -1 to -6, An is an anion, and B is a fibre-reactive group and the use thereof for dyeing hair.

Cationic reactive dyes

The present invention relates to new cationic reactive dyes and to their use in dyeing, especially their use in dyeing hair.

It is known, for example from WO 95/01772, WO 95/15144, EP 714 954 and EP 318 294, that cationic dyes can be used for dyeing protein-containing material, for example keratin, silk, cellulose or cellulose derivatives, and synthetic fibres, for example polyamides. Cationic dyes exhibit very brilliant shades. A disadvantage is their unsatisfactory fastness to hydrolysis, especially their fastness to washing (see: John F. Corbett: "The Chemistry of Hair-care Products," JSCD August 1976, p. 290).

Fibre-reactive radicals are also known and are described, for example, in Venkataraman "The Chemistry of Synthetic Dyes" volume 6, pages 1-209, Academic Press, New York, London 1972 and in US Patent 5,684,138.

The problem of the present invention was to provide further, especially brilliant, dyes for dyeing protein-containing material, such as keratin, wool, leather, silk, cellulose or polyamides, especially keratin-containing fibres, cotton or nylon, and more especially human hair, which dyes are distinguished especially by good fastness to washing properties.

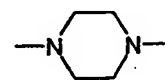
The present invention accordingly relates to cationic reactive dyes of the general formula



wherein

A is the radical of a cationic chromophore selected from the group of the acridine, anthraquinone, azine, azo, azomethine, benzimidazole, cyanine, diazo, dioxazine, ketoimine, methine, monoazo, nitro, oxazine, polymethine, quinoline, thiazole, triarylmethane and xanthene series,

D is  $-NR-$ ,  $-(NR'-(C_1-C_7\text{alkylene})-NR'')$  or a piperazinylene of formula



wherein

- 2 -

R is hydrogen, C<sub>1</sub>-C<sub>4</sub>alkyl, -CO-C<sub>1</sub>-C<sub>4</sub>alkyl, -CO-phenyl, ortho-, meta- or -para-(C<sub>6</sub>H<sub>4</sub>)-(C<sub>1</sub>-C<sub>4</sub>-alkyl), ortho-, meta- or para-(C<sub>6</sub>H<sub>4</sub>)-(C<sub>1</sub>-C<sub>4</sub>alkylene)-<sup>n</sup>N(R<sub>7</sub>R<sub>8</sub>R<sub>9</sub>), or -(C<sub>1</sub>-C<sub>4</sub>alkyl)-<sup>n</sup>N(R<sub>7</sub>R<sub>8</sub>R<sub>9</sub>), wherein

R<sub>7</sub>, R<sub>8</sub> and R<sub>9</sub> are each independently of the others hydrogen or C<sub>1</sub>-C<sub>4</sub>alkyl, and R' and R'' are each independently of the other hydrogen or C<sub>1</sub>-C<sub>4</sub>alkyl, m is an integer 0 or 1, and

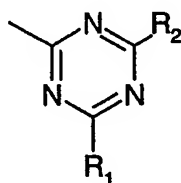
x is an integer from 1 to 8, preferably 1 or 2 and more especially 1,

n<sup>+</sup> is the charge of the radical [A-(D<sub>m</sub>-B)<sub>x</sub>] and is an integer from +1 to +6, preferably +1 or +2 and more especially +1,

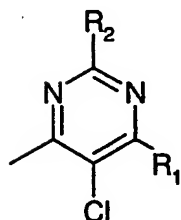
n<sup>-</sup> is the charge of the anion and is an integer from -1 to -6, preferably -1 or -2 and more especially -1,

An is an anion, and

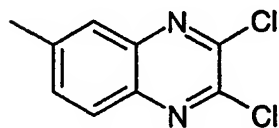
B is a fibre-reactive group of formula (2a), (2b) or (2c), or (2d), (2e), (2f) or (2g), and preferably, when m is 1, B denotes a fibre-reactive group of formula (2a), (2b) or (2c),



(2a),

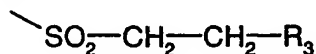


(2b) or

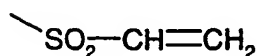


(2c)

or, when m is 0, B denotes a fibre-reactive group of formula (2d), (2e), (2f) or (2g),

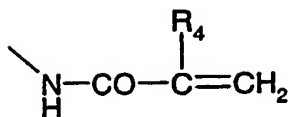


(2d),

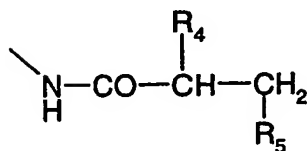


(2e),

- 3 -



(2f) or

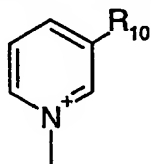


(2g),

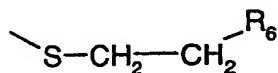
wherein

 $\text{R}_3$  is  $-\text{OSO}_3\text{X}$ ,  $-\text{OSO}_3^-$  or  $-\text{Cl}$ , $\text{R}_4$  and  $\text{R}_5$  are each independently of the other  $-\text{Cl}$  or  $-\text{Br}$ , and $\text{R}_1$  and  $\text{R}_2$  are each independently of the other  $-\text{Cl}$ ,  $-\text{F}$ ,

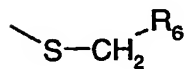
or the radical of a compound of formula (3a), (3b), (3c), (3d), (3e), (3f) or (3g),



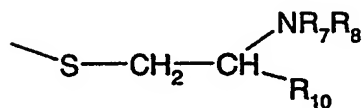
(3a),



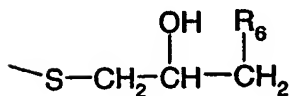
(3b),



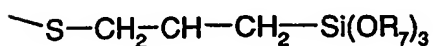
(3c),



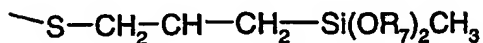
(3d),



(3e),



(3f) or



(3g),

wherein

 $\text{R}_6$  is  $\text{SO}_3^-$ ,  $\text{SO}_3\text{X}$ ,  $\text{O}^-$ ,  $\text{OX}$ ,  $\text{COO}^-$ ,  $\text{COOX}$  or  $^+\text{N(R}_7\text{ R}_8\text{ R}_9)\text{An}^-$ , $\text{X}$  is hydrogen or a cation of an alkali metal or alkaline earth metal, $\text{R}_7$ ,  $\text{R}_8$  and  $\text{R}_9$  are each independently of the others hydrogen or  $\text{C}_1\text{--C}_4$ alkyl,



An<sup>-</sup> is an anion, and

R<sub>10</sub> is COO<sup>-</sup> or COOX,

wherein, when x > 1 is, B denotes identical or not identical fibre-reactive groups.

Alkyl and alkylene may be straight-chain, branched, monocyclic or polycyclic.

Alkylene is generally an alkylene radical having from 1 to 7 carbon atoms, for example C<sub>1</sub>-C<sub>7</sub>alkylene that is methylene, dimethylene, n-propylene, 1-methyl-methylene, 1,1-dimethyl-methylene, 1,1-dimethyl-dimethylene, 1-ethyl-dimethylene, n-butylene, 1-ethyl-1-methyl-dimethylene, n-pentylene, 1,1-dimethyl-propylene, 2,2-dimethyl-propylene, 1-ethyl-propylene, 2-ethyl-propylene, 2-methylbutylene, n-hexylene, 2,2-dimethyl-butylene, n-heptylene, 3,3-dimethyl-butylene, 2,2-dimethyl-butylene, or 1-ethyl-butylene, 2-ethyl-butylene, or 1-ethyl-butylene.

The alkylene radicals can be interrupted by at least one hetero atom, for example -O-, -S-, -NH- or -N(C<sub>1</sub>-C<sub>12</sub>alkyl)-.

C<sub>1</sub>-C<sub>4</sub>Alkyl is, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl or cyclobutyl.

C<sub>1</sub>-C<sub>12</sub>Alkyl is, for example, C<sub>1</sub>-C<sub>4</sub>alkyl as defined above and also n-pentyl, 2-pentyl, 3-pentyl, 2,2-dimethylpropyl, cyclopentyl, cyclohexyl, n-hexyl or dimethylbutyl, n-heptyl, n-octyl, 1,1,3,3-tetramethylbutyl, 2-ethylhexyl, nonyl, trimethylcyclohexyl, decyl, menthyl, thujyl, bornyl, 1-adamantyl, 2-adamantyl or dodecyl.

C<sub>1</sub>-C<sub>4</sub>Alkoxy is, for example, methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy or tert-butoxy.

C<sub>1</sub>-C<sub>4</sub>Alkoxy carbonyl is, for example, methoxycarbonyl, ethoxycarbonyl, n-propoxycarbonyl, isopropoxycarbonyl, n-butoxycarbonyl or tert-butoxycarbonyl.

Anion, or An, denotes, for example, inorganic or organic anions, such as halide, for example chloride, bromide or iodide, sulfate, hydrogen sulfate, methylsulfate, borotetrafluoride,

aminosulfonate, perchlorate, carbonate, bicarbonate, phosphate, nitrate, benzenesulfonate, formate, acetate, propionate, lactate, or complex anions, such as the anion of zinc chloride double salts.

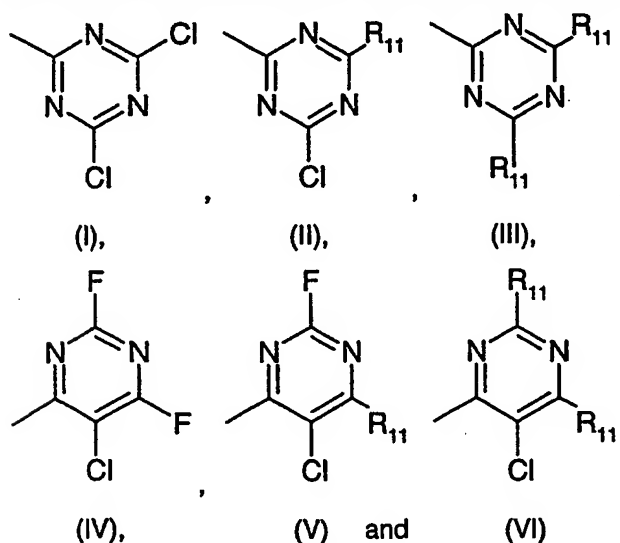
The anion is generally determined by the preparation process. Preferably, the chlorides, hydrogen sulfates, sulfates, methosulfates, phosphates, formates, lactates or acetates are present.

Halogen is, for example, fluorine, chlorine, bromine or iodine, especially fluorine and preferably chlorine.

Alkali metal is, for example, lithium, sodium or potassium.

Alkaline earth metal is, for example, magnesium, calcium, strontium or copper, zinc or aluminium.

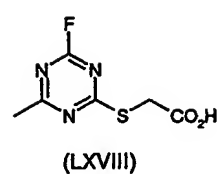
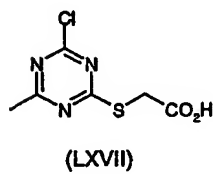
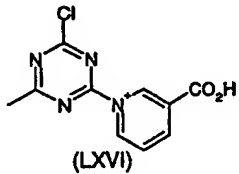
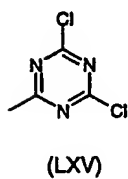
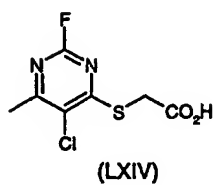
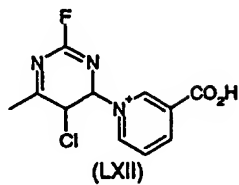
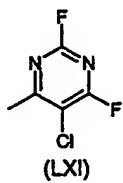
Of particular interest are cationic reactive dyes of formula (1) wherein x is a number from 1 to 8, and B is a radical of a fibre-reactive group of formula (2a) or (2b), especially a radical of a fibre-reactive group selected from the group of compounds of formulae



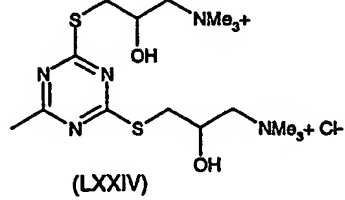
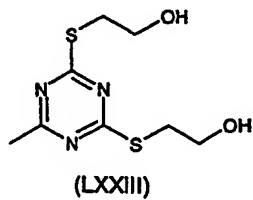
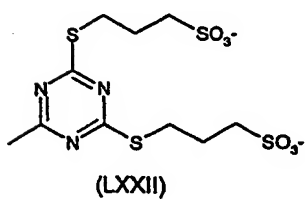
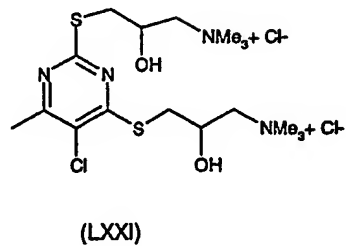
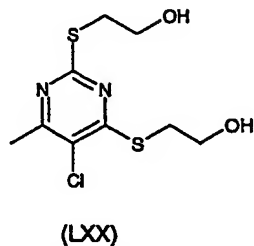
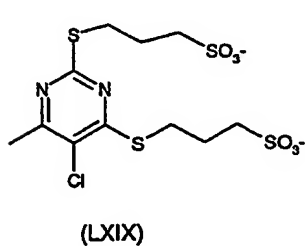
wherein

R<sub>11</sub> is a radical of a compound of formulae (3a) to (3g).

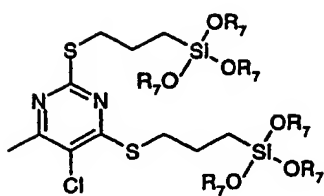
As radicals of fibre-reactive groups special preference is given to compounds of formulae (LXI)-(LXVIII),



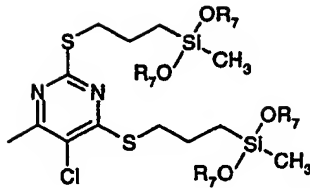
and to dithiopyrimidines and dithiotriazines of formulae (LXIX)-(LXXIV)



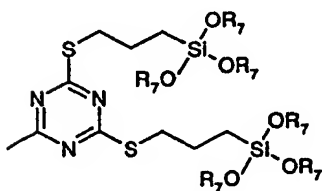
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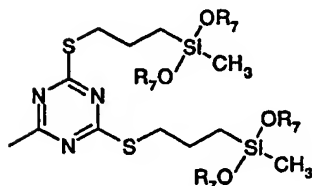
(LXXX)



(LXXXI)



(LXXXII)



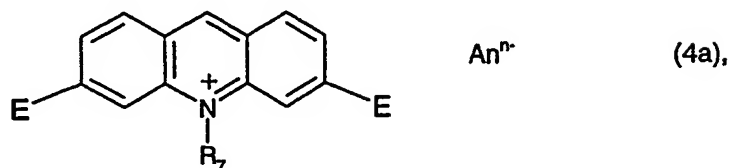
(LXXXIII)

wherein

$R_7$  is as defined above.

Preferred cationic reactive dyes are

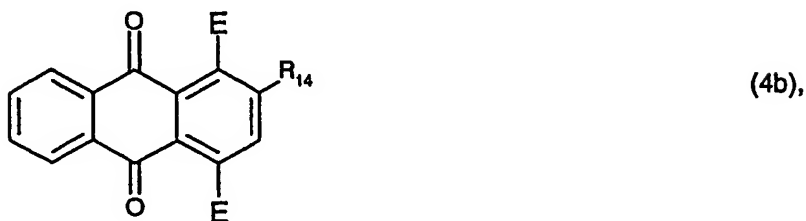
a) acridines of formula



wherein

$R_7$  and  $An^{n+}$  are as defined above;

b) anthraquinones of formula

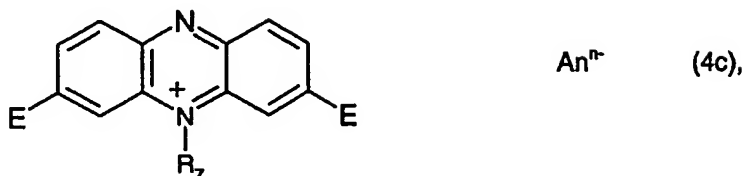


wherein

$R_{14}$  is  $-S-(C_1-C_4)-^+NR_7R_8R_9$ ,  $An^{n+}$ , preferably  $-S-(ethylene)-^+N(CH_3)_3$ ,  $An^{n+}$ , and

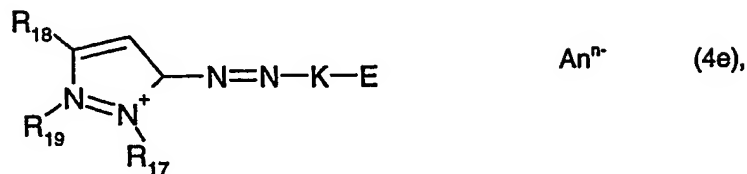
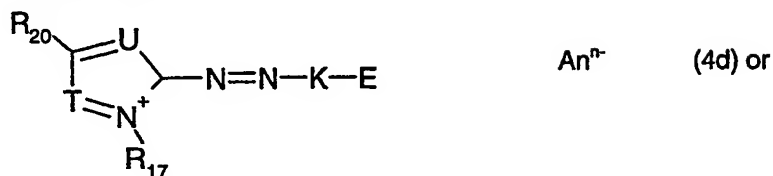
An,  $n^-$ ,  $R_7$ ,  $R_8$  and  $R_9$  are as defined above;

c) azines of formula



wherein  $R_7$ ,  $n^-$  and An are as defined above;

d) azo compounds of formula



wherein

U is -O-, -S- or -NR<sub>17</sub>,

T is -CH=, -CR<sub>17</sub>= or -N=,

$R_{17}$  and  $R_{19}$  are each independently of the other C<sub>1</sub>-C<sub>4</sub>alkyl unsubstituted or substituted by OH, C<sub>1</sub>-C<sub>4</sub>alkoxy, halogen, CN, amino, C<sub>1</sub>-C<sub>4</sub>monoalkylamino or by di-C<sub>1</sub>-C<sub>4</sub>alkylamino,

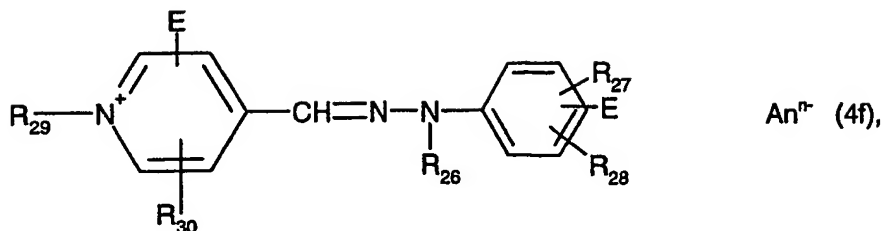
$R_{18}$  is hydrogen, C<sub>1</sub>-C<sub>4</sub>alkyl, chlorine or nitro,

$R_{20}$  is hydrogen, C<sub>1</sub>-C<sub>4</sub>alkyl, chlorine, nitro, amino, C<sub>1</sub>-C<sub>4</sub>monoalkylamino or di-C<sub>1</sub>-C<sub>4</sub>alkylamino,

K is the radical of a coupling component from the aniline or phenol series or the radical of a heterocyclic coupling component, and

$n^-$  and An are as defined above;

d) azomethines of formula



wherein

R<sub>30</sub> is hydrogen, C<sub>1</sub>-C<sub>4</sub>alkyl or CN,

R<sub>29</sub> is C<sub>1</sub>-C<sub>4</sub>alkyl unsubstituted or substituted by OH or by CN,

R<sub>28</sub> is hydrogen or C<sub>1</sub>-C<sub>4</sub>alkyl,

R<sub>27</sub> and R<sub>28</sub> are each independently of the other hydrogen, C<sub>1</sub>-C<sub>4</sub>alkyl or C<sub>1</sub>-C<sub>4</sub>alkoxy, or

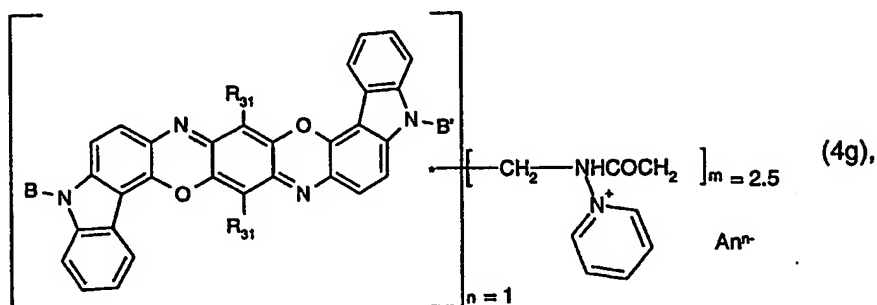
R<sub>27</sub> is fluorine in the ortho position, with R<sub>30</sub> and R<sub>28</sub> being hydrogen and R<sub>29</sub> and R<sub>26</sub> being methyl, or

R<sub>27</sub> is chlorine in the para position, with R<sub>30</sub> and R<sub>28</sub> being hydrogen and R<sub>29</sub> and R<sub>26</sub> being methyl, or

R<sub>26</sub> and R<sub>27</sub> together with the nitrogen and carbon atoms bonding them form a 5- or 6-membered ring, and

n<sup>+</sup> and An<sup>n+</sup> are as defined above;

e) dioxazines of formula



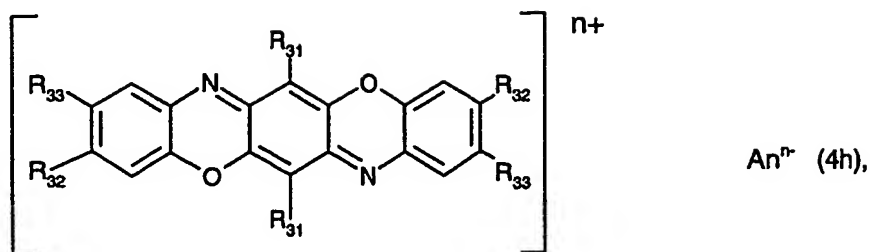
wherein

B' is B or hydrogen, and

R<sub>31</sub> is hydrogen, halogen, C<sub>1</sub>-C<sub>24</sub>alkyl or E,

n<sup>+</sup> and An<sup>n+</sup> are as defined above;

or dioxazines of formula

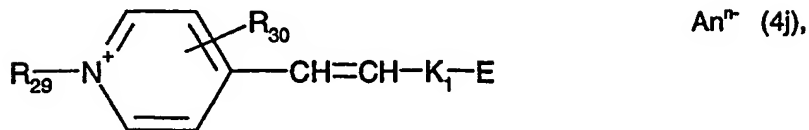
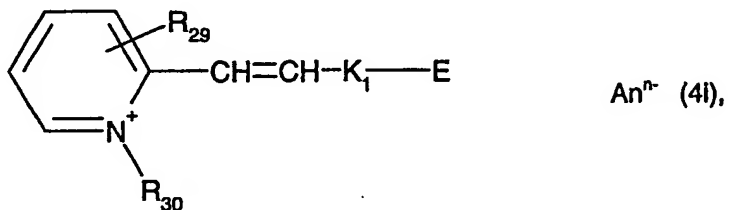


wherein

R<sub>31</sub>, R<sub>32</sub> and R<sub>33</sub> are each independently of the others hydrogen, halogen, C<sub>1</sub>-C<sub>4</sub>alkyl, C<sub>1</sub>-C<sub>4</sub>-alkoxy or E, and

n<sup>+</sup> and An are as defined above;

f) methines of formulae



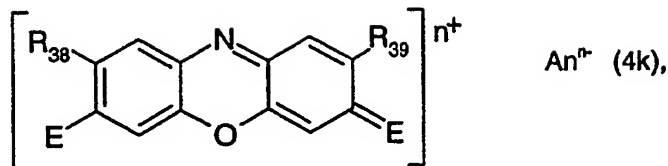
wherein

R<sub>29</sub>, R<sub>30</sub>, n<sup>+</sup> and An are as defined above, and

K<sub>1</sub> is the radical of an aromatic or heterocyclic amine;

g) oxazines of formula

- 11 -



wherein

$R_{38}$  and  $R_{39}$  are each independently of the other E,  $C_1$ - $C_4$ alkyl or  $C_1$ - $C_4$ alkoxy, and  $n$ ,  $n^+$  and An are as defined above;

and, in the above-mentioned formulae, E is in each case ( $D_m$ -E'), wherein

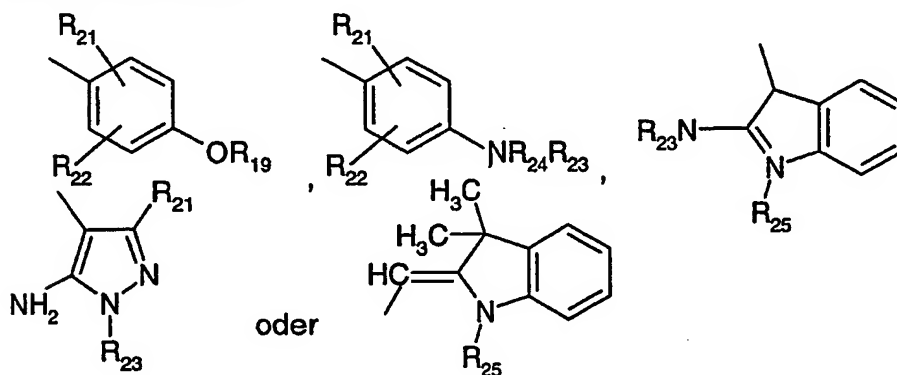
D and m are as defined above, and

E' is hydrogen or B,

with the proviso that E in each formula is at least once ( $D_m$ -E') wherein

E' is B, and B has the definitions or preferences given above.

In the dyes of formulae (4d) and (4e), the radicals -K-E together form a compound of the formulae given below



wherein

$R_{19}$  is hydrogen or B, or  $C_1$ - $C_4$ alkyl unsubstituted or substituted by E, OH,  $C_1$ - $C_4$ alkoxy, halogen, CN, amino,  $C_1$ - $C_4$ monoalkylamino or by di- $C_1$ - $C_4$ alkylamino,

$R_{21}$  and  $R_{22}$  are each independently of the other E, OH,  $C_1$ - $C_4$ alkoxy, halogen, CN, amino,  $C_1$ - $C_4$ monoalkylamino or by di- $C_1$ - $C_4$ alkylamino, or  $C_1$ - $C_4$ alkyl unsubstituted or substituted by E, OH,  $C_1$ - $C_4$ alkoxy, halogen, CN, amino,  $C_1$ - $C_4$ monoalkylamino or by di- $C_1$ - $C_4$ alkylamino,



- 12 -

$R_{23}$  and  $R_{24}$  are each independently of the other hydrogen or B, or C<sub>1</sub>-C<sub>4</sub>alkyl unsubstituted or substituted by OH, C<sub>1</sub>-C<sub>4</sub>alkoxy, halogen, CN, amino, C<sub>1</sub>-C<sub>4</sub>monoalkylamino or by di-C<sub>1</sub>-C<sub>4</sub>alkylamino, or

$R_{23}$  and  $R_{24}$  together with the nitrogen atom bonding them form a 5- or 6-membered ring unsubstituted or substituted by E, or

$R_{21}$  and  $R_{23}$  together with the nitrogen and carbon atoms bonding them form a 5- or 6-membered ring unsubstituted or substituted by E, or

$R_{22}$  and  $R_{24}$  together with the nitrogen and carbon atoms bonding them form a 5- or 6-membered ring unsubstituted or substituted by E, and

$R_{25}$  is hydrogen or B, or C<sub>1</sub>-C<sub>4</sub>alkyl unsubstituted or substituted by E, OH, C<sub>1</sub>-C<sub>4</sub>alkoxy, halogen, CN, amino, C<sub>1</sub>-C<sub>4</sub>monoalkylamino or by di-C<sub>1</sub>-C<sub>4</sub>alkylamino, and

E is in each case ( $D_m-E'$ ), wherein

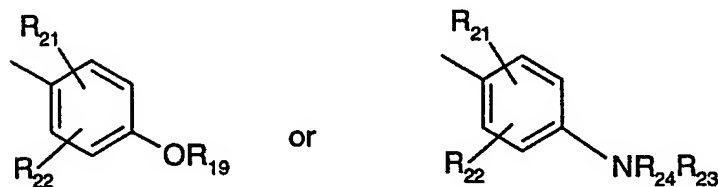
D and m are as defined above, and

E' is hydrogen or B,

with the proviso that E in each formula is at least once ( $D_m-E'$ ) wherein

E' is B, and B has the definitions or preferences given above.

For the radicals -K-E special preference is given to a compound of formula



wherein

$R_{19}$  is hydrogen or B, or unsubstituted C<sub>1</sub>-C<sub>4</sub>alkyl,

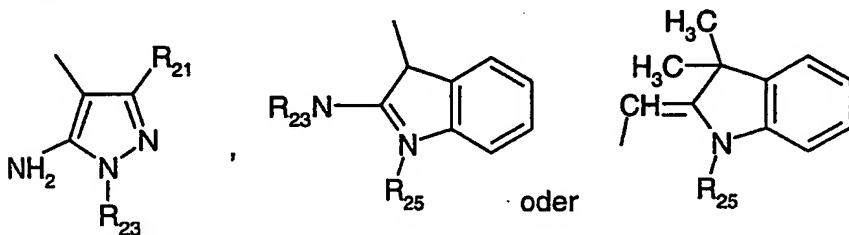
$R_{21}$  and  $R_{22}$  are each independently of the other hydrogen, E, unsubstituted C<sub>1</sub>-C<sub>4</sub>alkyl, C<sub>1</sub>-C<sub>4</sub>alkoxy or halogen,

$R_{23}$  and  $R_{24}$  are each independently of the other hydrogen or B, or unsubstituted C<sub>1</sub>-C<sub>4</sub>alkyl, or

$R_{23}$  and  $R_{24}$  together with the nitrogen atom bonding them form a pyrrolidine, piperidine, morpholine or piperazine ring unsubstituted or substituted by E, or

$R_{21}$  and  $R_{23}$  together with the nitrogen atom and carbon atom bonding them form a pyrrolidine, piperidine, morpholine or piperazine ring unsubstituted or substituted by E, or  $R_{22}$  and  $R_{24}$  together with the nitrogen atom and carbon atom bonding them form a pyrrolidine, piperidine, morpholine or piperazine ring unsubstituted or substituted by E; and E is in each case ( $D_m-E'$ ), wherein D and m are as defined above, and E' is hydrogen or B, with the proviso that E in each formula is at least once ( $D_m-E'$ ) wherein E' is B, and B has the definitions or preferences given above.

In the cationic reactive dyes of formulae (4i) and (4j), the radicals  $-K_1-E$  together form a compound of formula



wherein

$R_{21}$  is E, C<sub>1</sub>-C<sub>4</sub>alkyl, C<sub>1</sub>-C<sub>4</sub>alkoxy or halogen,  $R_{23}$  and  $R_{25}$  are each independently of the other hydrogen or B, or C<sub>1</sub>-C<sub>4</sub>alkyl unsubstituted or substituted by OH, C<sub>1</sub>-C<sub>4</sub>alkoxy, halogen, CN, amino, C<sub>1</sub>-C<sub>4</sub>monoalkylamino or by di-C<sub>1</sub>-C<sub>4</sub>alkylamino, and

E is in each case ( $D_m-E'$ ), wherein D and m are as defined above, and E' is hydrogen or B, with the proviso that E in each formula is at least once ( $D_m-E'$ ) wherein E' is B, and B has the definitions or preferences given above.

The cationic charge of the chromophore can be localised or delocalised.

The cationic charge is localised when it is not directly adjacent, i.e. in the  $\alpha$ -position, to a double bond. The cationic charge is delocalised when it is adjacent, i.e. in the  $\alpha$ -position, to a double bond.

Cationic chromophores having a delocalised or localised charge are known, for example, from the Colour Index. The corresponding chromophores are described therein as C.I. Basic Dyes. Such chromophores can be used in principle as basic structures for cationic reactive dyes, with at least one reactive group being introduced, where appropriate after the prior introduction of the bridging member.

Suitable C.I. Basic Dyes are, for example, C.I. Basic Yellow 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54 and 55, and

C.I. Basic Orange 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47 and 48, and

C.I. Basic Red 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70 and 71, and

C.I. Basic Violet 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40 and 41, and


C.I. Basic Blue 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97 and 98, and

C.I. Basic Green 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10, and

C.I. Basic Brown 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14 and 15, and

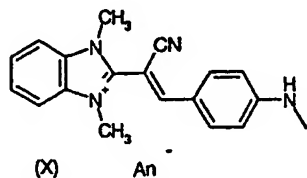
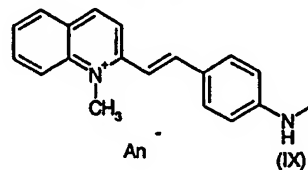
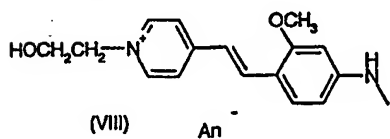
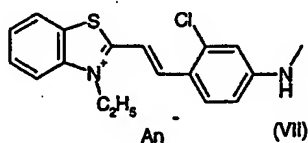
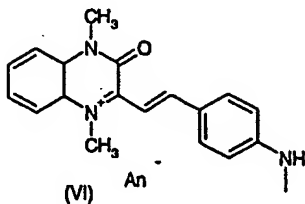
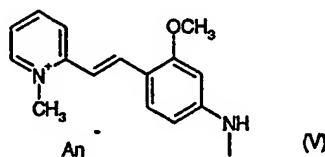
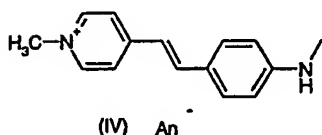
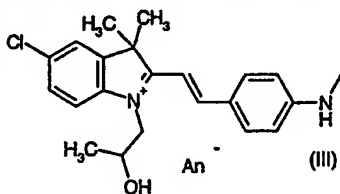
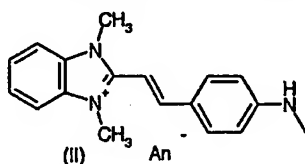
C.I. Basic Black C.I. 1, 2, 3, 4, 5, 6, 7 and 8.

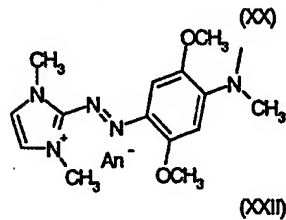
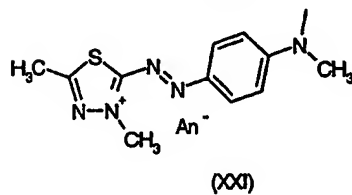
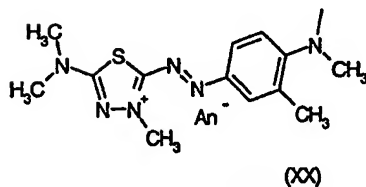
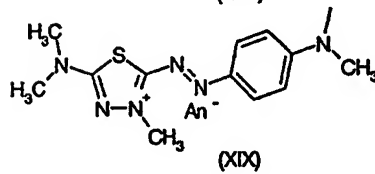
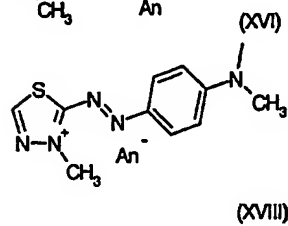
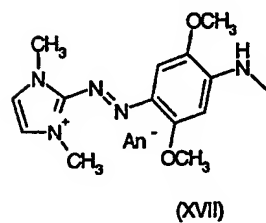
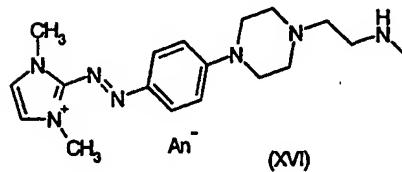
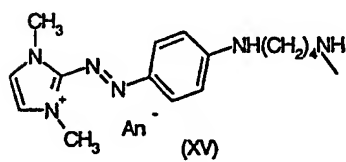
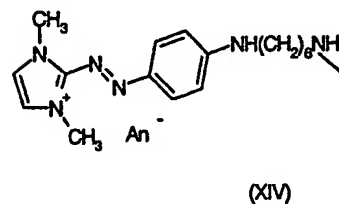
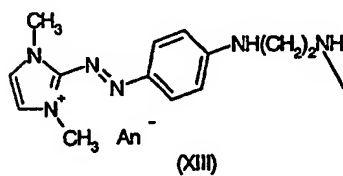
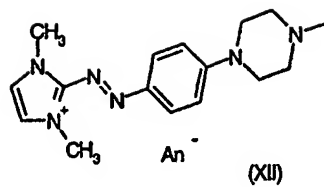
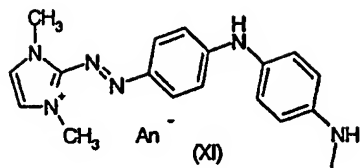
Special preference is given to radicals of cationic chromophores that have a delocalised cationic charge, especially cationic azo, azomethine, dioxazine, methine, monoazo and oxazine chromophores.

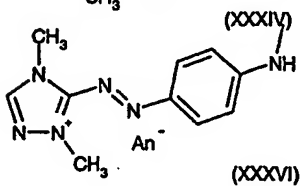
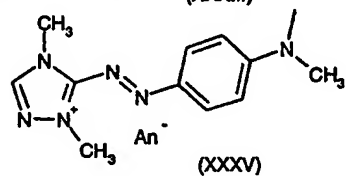
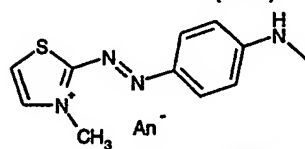
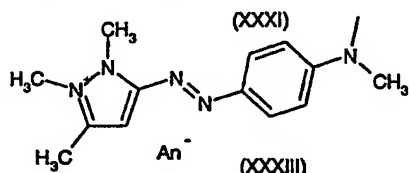
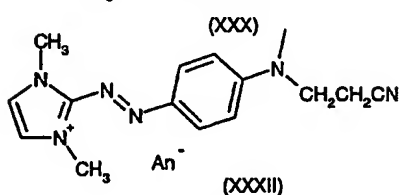
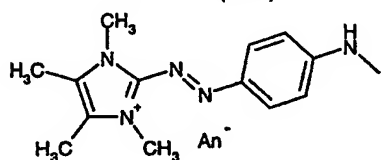
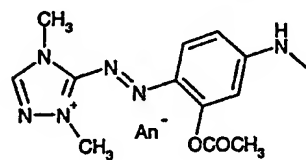
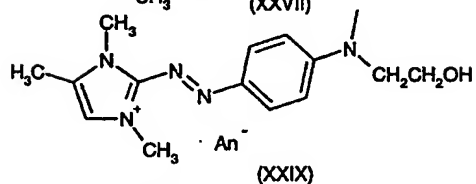
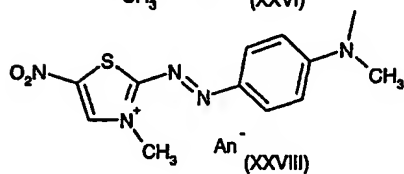
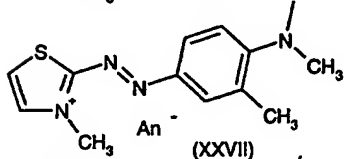
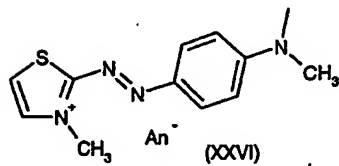
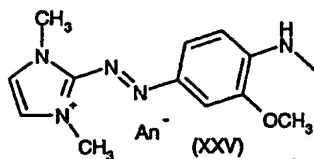
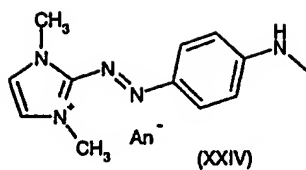
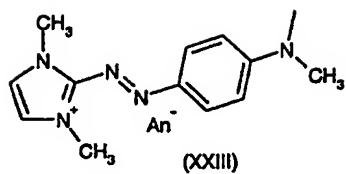
Very special preference is given to radicals of cationic chromophores that have a delocalised cationic charge and are bonded, by way of the radical of their piperazinylene substituent of formula  or the radical of their diaminoalkylene substituent of formula

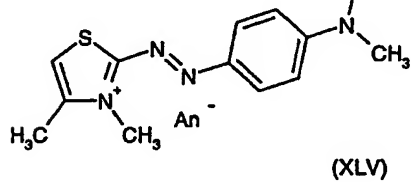
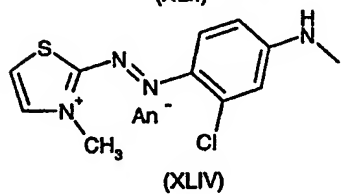
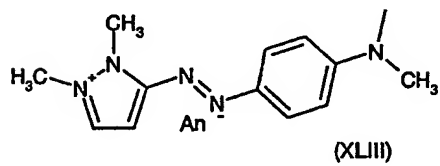
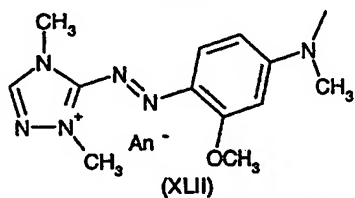
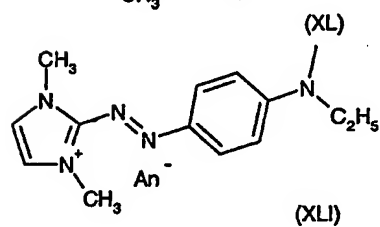
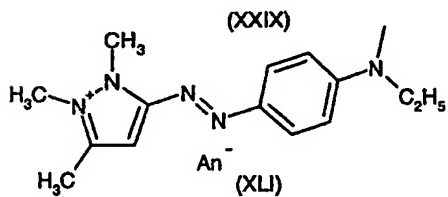
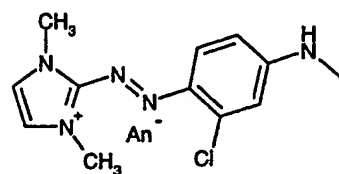
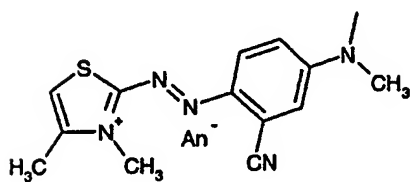
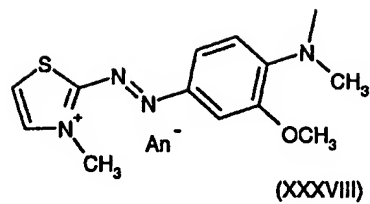
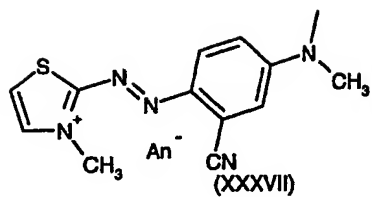
-(NR'-(C<sub>1</sub>-C<sub>7</sub>alkylene)-NR'')-, or of their -NR- or -NH- substituent, wherein R, R' and R'' are as defined above,

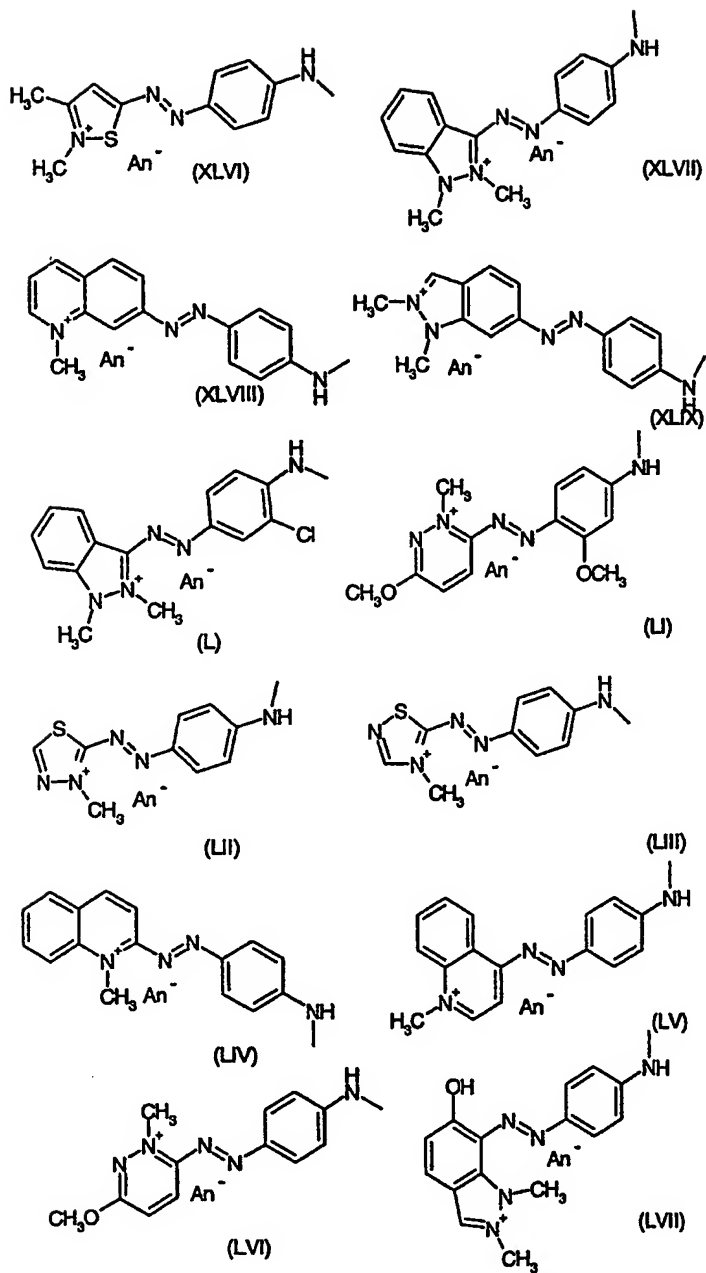
to the radical of a fibre-reactive group, for example compounds of formulae (II) - (LX)





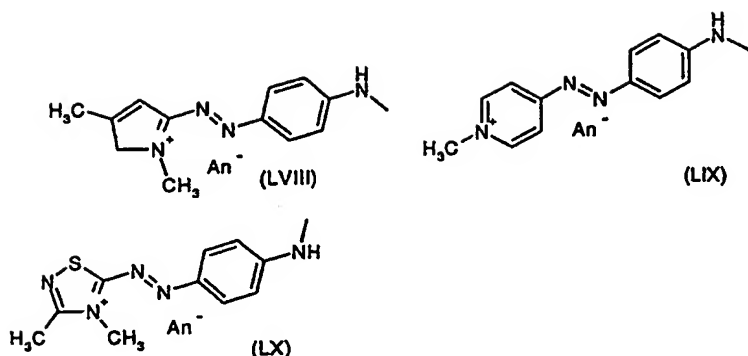








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wherein

An is as defined above.

In the present invention, preference is given to cationic reactive dyes of the general formula

$$[A_1-B]^+ An^- \quad (1a),$$

wherein

A<sub>1</sub> is a compound of formula (II)-(LX), and

B is the radical of a fibre-reactive group of formula (2a) wherein

R<sub>1</sub> and R<sub>2</sub> are each independently of the other -Cl, or the radical of a compound of formula (3a), (3b), (3c), (3d), (3e), (3f) or (3g),

and R<sub>1</sub> and R<sub>2</sub> are preferably -Cl,

or

B is the radical of a fibre-reactive group of formula (2b) wherein

R<sub>1</sub> and R<sub>2</sub> are each independently of the other fluorine or the radical of a compound of formula (3a), (3b), (3c), (3d), (3e), (3f) or (3g),

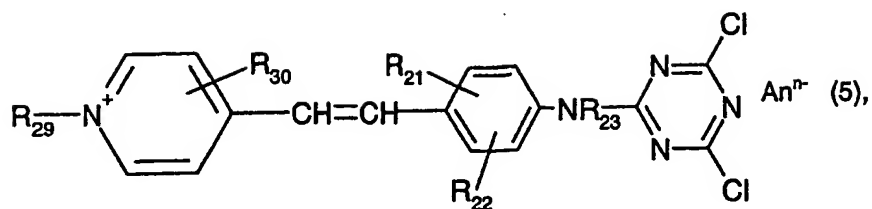
and preferably R<sub>2</sub> is fluorine and R<sub>1</sub> is fluorine or the radical of a compound of formula (3a), (3b), (3c), (3d), (3e), (3f) or (3g), and

An is as defined above,

and is preferably chloride, methylsulfate or ethylsulfate.

Special preference is given to cationic reactive dyes of formula

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wherein

$R_{21}$  and  $R_{22}$  are each independently of the other hydrogen,  $C_1$ - $C_4$ alkyl,  $C_1$ - $C_4$ alkoxy or halogen,

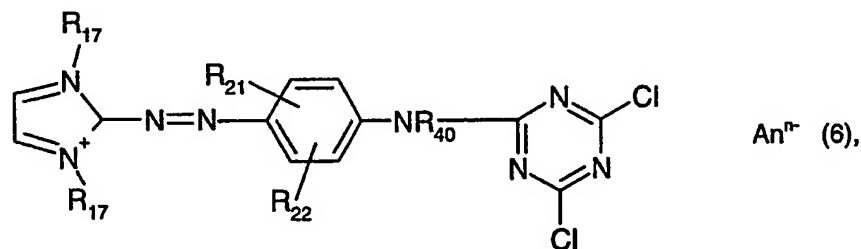
$R_{23}$  is hydrogen or unsubstituted  $C_1$ - $C_4$ alkyl,

$R_{29}$  is  $C_1$ - $C_4$ alkyl unsubstituted or substituted by OH or by CN, and

$R_{30}$  is hydrogen,  $C_1$ - $C_4$ alkyl or CN, and

An and  $n^-$  are as defined above,

and to cationic reactive dyes of formula

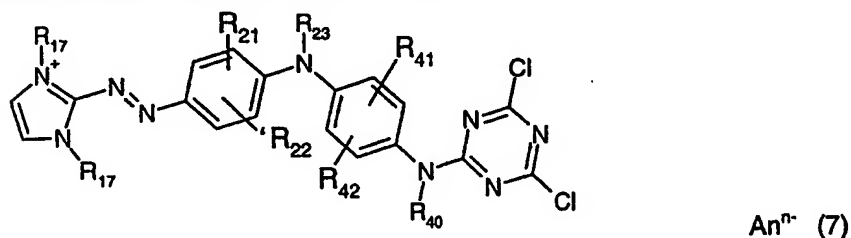


wherein

$R_{17}$  and  $R_{40}$  are each independently of the other hydrogen, or  $C_1$ - $C_4$ alkyl unsubstituted or substituted by OH,  $C_1$ - $C_4$ alkoxy, halogen, CN, amino,  $C_1$ - $C_4$ monoalkylamino or by di- $C_1$ - $C_4$ alkylamino, and

An and  $n^-$ ,  $R_{21}$  and  $R_{22}$  are as defined above,

and to cationic reactive dyes of formula

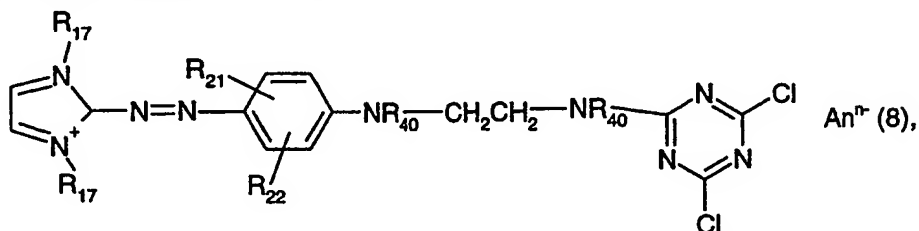


wherein

An,  $n^-$ ,  $R_{17}$ ,  $R_{40}$ ,  $R_{21}$ ,  $R_{22}$  and  $R_{23}$  are as defined above, and

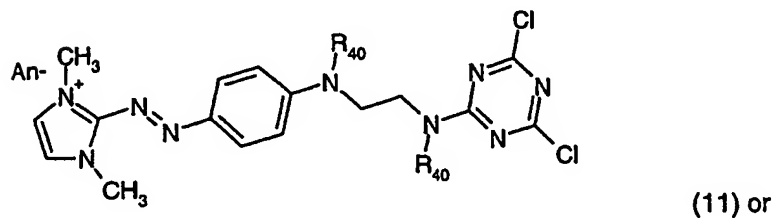
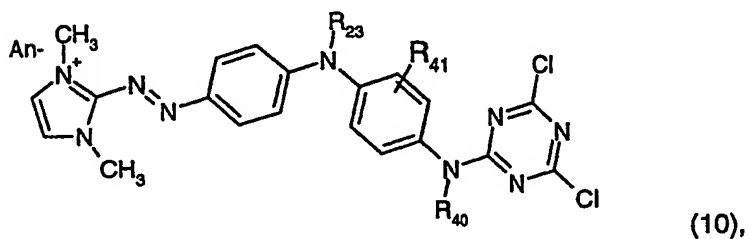
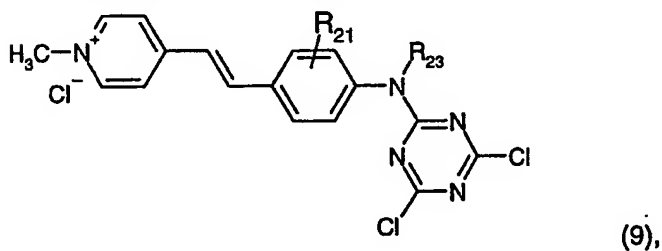
$R_{40}$  and  $R_{41}$  are each independently of the other hydrogen, or  $C_1$ - $C_4$ alkyl unsubstituted or substituted by OH,  $C_1$ - $C_4$ alkoxy, halogen, CN, amino,  $C_1$ - $C_4$ monoalkylamino or by di- $C_1$ - $C_4$ alkylamino, and

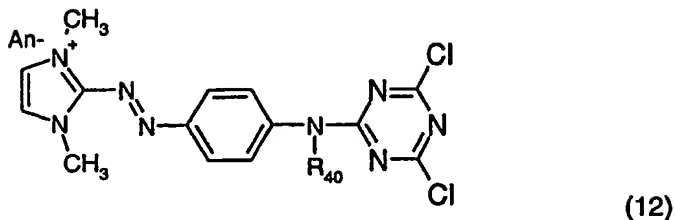
to cationic reactive dyes of formula



wherein  $R_{17}$ ,  $R_{21}$ ,  $R_{22}$ ,  $R_{40}$ , An and  $n^-$  are as defined above.

Very special preference is given to a cationic reactive dye of formula (9), (10), (11) or (12)





wherein

$R_{21}$ ,  $R_{23}$ ,  $R_{40}$ ,  $R_{41}$  and An are as defined above.

The present invention relates also to a process for the preparation of cationic reactive dyes of formula (1), in which process a cationic chromophore A is reacted with x fibre-reactive groups B and where appropriate with m bridging members D, wherein the definitions and preferred meanings given above for A, B, D, x and m apply.

A preferred embodiment of the present invention relates to a process for the preparation of cationic reactive dyes of formula (1)

wherein

A is the radical of a cationic chromophore, and

D is  $-NR-$ , wherein

the definitions and preferred meanings given above for B, x,  $n^-$ ,  $n^+$ , An and m apply,

in which process a cationic chromophore A is reacted with x fibre-reactive groups B.

The reaction is usually initiated by bringing the fibre-reactive group into contact with the cationic chromophore in accordance with methods known *per se*, for example by mixing the starting materials or adding one starting material dropwise to the other. Preferably the fibre-reactive group is added to the cationic chromophore.

In order to prepare compounds of formula (1), a molar ratio of fibre-reactive group to cationic chromophore is generally selected in the range from 2:1 to 0.5:1, preferably in the range from 1:1 to 0.5:1, especially in the range from 0.8:1 to 0.5:1. If more than one fibre-reactive group is being introduced, the molar ratio should be adjusted accordingly.

The reaction temperature during the addition of a starting material is preferably selected in the range from -10 to + 30°C, preferably in the range from -5 to +20°C, especially in the range from -2 to +2°C.

The reaction temperature after the addition of a starting material is preferably selected in the range from 0 to +40°C, preferably in the range from +5 to +25°C.

The reaction pressure is generally selected in the range from 70 kPa to 10 MPa, preferably from 90 kPa to 5 MPa, and is especially atmospheric pressure.

The reaction time generally depends upon the reactivity of the starting materials, the reaction temperature selected and the desired conversion. The reaction time is generally selected in the range of from 15 minutes to several hours.

In a preferred embodiment, the reaction is carried out under a protecting gas atmosphere; for that purpose it is preferred to use nitrogen or a noble gas, such as helium or argon. The reaction is especially carried out in a nitrogen atmosphere.

The reaction can also be carried out with or without solvent; the reaction is preferably carried out in a solvent. Preference is given to water or to an organic solvent or mixture of solvents with or without water. Preferred organic solvents are protic and aprotic solvents.

Aprotic solvents can be apolar, such as benzene, chlorobenzene, chlorinated hydrocarbons, or polar. The latter are especially preferred.

As polar aprotic solvents there can be used, for example, amides, such as hexamethylphosphoric acid triamide, carboxamides, such as N,N'-dimethylformamide, N,N'-dimethylacetamide, and lactams, such as N-methylpyrrolidone, N-methyl-2-piperidone, 1,3-dimethyl-3,4,5,6-tetrahydro-3(1H)pyrimidinone and N-methyl-4-piperidone, and urea bases, such as N,N'-dimethylethyleneurea, N,N'-dimethylpropyleneurea and acetonitrile, sulfolans, dimethyl sulfoxide and aromatic solvents, such as nitrobenzene.

As protic solvent there may be mentioned, preferably, water.

The ratio by weight of cationic chromophore to solvent is generally in the range from 0.5 to 20 % by weight, especially in the range from 1 to 10 % by weight and more especially in the range from 2 to 8 % by weight.

It is generally advisable to carry out the reaction in the presence of a base. Suitable bases are, for example, alkali metal carbonates, e.g.  $\text{Na}_2\text{CO}_3$  or  $\text{K}_2\text{CO}_3$ , alkali metal hydrogen carbonates, for example  $\text{NaHCO}_3$  or  $\text{KHCO}_3$ , alkali metal hydroxides, for example  $\text{NaOH}$  or  $\text{KOH}$ , alkali metals, for example sodium or potassium, and aromatic bases, such as pyridine,  $N,N'$ -dimethylaminopyridine or quinoline. Preference is given to non-aqueous alkali metal bases and to aromatic bases, special preference is given to non-aqueous alkali metal carbonates and alkali metal hydrogen carbonates and very special preference is given to non-aqueous  $\text{K}_2\text{CO}_3$ .

The molar ratio of base to cationic chromophore is usually in the range from 2:1 to 0.5:1, preferably in the range from 1:1 to 0.5:1, especially in the range from 0.8:1 to 0.5:1.

In a preferred embodiment of the process according to the invention, the reaction is carried out in the presence of water and a base.

It has proved advantageous to keep the pH of the reaction mixture constant during the addition of a starting material by adding a base. Preference is given to a pH in the range from pH 3 to pH 5 and especially from 3.5 to 4.5.

The reaction mixture can be worked up according to customary methods, for example by filtration and then washing the filter residue and, optionally, subsequent drying.

It is also possible, however, to adjust the reaction mixture comprising the cationic reactive dye to pH 6 by adding a base, and to use the resulting reaction mixture, preferably the resulting dyeing solution, for dyeing keratin-containing fibres.

A further preferred embodiment of the present invention relates to a process for the preparation of cationic reactive dyes of formula (1),

wherein

A is the radical of a cationic chromophore, and

D is  $-(NR'-(C_1-C_7\text{alkylene})-NR'')$ , or a piperazinylene of formula , wherein the

definitions and preferred meanings given above for R', R'', alkylene, B, x, n<sup>-</sup>, n<sup>+</sup>, An and m apply,

in which process a cationic chromophore A is reacted with m bridging members D, and then the resulting reaction mixture is reacted with x fibre-reactive groups B.

Usually the reaction is initiated by bringing the cationic chromophore into contact with diaminoalkylene or piperazine and with the fibre-reactive group according to methods known *per se*, for example by mixing the starting materials or adding one starting material dropwise to the other. Preferably the cationic chromophore is first reacted with diaminoalkylene or piperazine, and then the fibre-reactive group is added to the reaction mixture.

Generally, the molar ratio of diaminoalkylene or piperazine to cationic chromophore is selected in the range from 0.8:1 to 0.3:1. When more than one bridging member is being introduced, the molar ratios should be adjusted accordingly.

It has proved advantageous to carry out the reaction of diaminoalkylene or piperazine with the cationic chromophore in the range of the pKa value of the piperazine or diaminoalkylene being reacted.

In a preferred embodiment of the present invention, the reaction with the fibre-reactive group generally follows the reaction of the cationic chromophore with the diaminoalkylene or piperazine.

A preferred embodiment of the present invention relates to dyeing solutions obtainable according to the processes of the invention.

In addition, the present invention relates to a dye composition, preferably a dyeing solution, comprising at least a single cationic reactive dye.

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Preferably the present invention relates to a dye composition, preferably a dyeing solution, comprising

- a) at least one cationic reactive dye of formula (1),
- b) a medium for adjusting the pH,
- c) water,
- and, optionally,
- d) further additives.

The multiplicity of shades of the dye, which results by the method according to the present invention, can be increased by combination with other dyes.

The present invention relates also to the colouration of hair with a dye, which results by the method according to the present invention, and at least one other dye.

The dye, which results by the combination of at least one capped diazonium compound and at least one coupling compound, can be combined with dyes of the same or different class of dyes, especially with direct dyes, oxidation dyes; dye precursor combinations of a coupler compound and a diazotized compound, or a capped diazotized compound; and/or cationic reactive dyes.

Direct dyes are natural or synthetic, they are uncharged, cationic or anionic, such as acid dyes.

Oxidation dye denotes also for oxidation dye precursors, which are from the group of the developer and coupler compounds.

In the context of the invention the single classes of dyes comprise the dyes defined in the Color Index of the Society of Textile Chemist and Colorist.

Preferably the compositions, formulations, methods and processes comprise at least a single cationic reactive dye.



In the following suitable direct dyes for the combination with the method according to the present invention are described.

Directs dyes are for example described in "Dermatology", edited by Ch. Culnan, H. Maibach, Verlag Marcel Dekker Inc., New York, Basle, 1986, Vol. 7, Ch. Zviak, The Science of Hair Care, chapter 7, pages 248-250, and in "Europäisches Inventar der Kosmetikrohstoffe", 1996, published by The European Commission, obtainable in diskette form from the Bundesverband der deutschen Industrie- und Handelsunternehmen für Arzneimittel, Reformwaren und Körperpflegemittel e.V., Mannheim.

Preferred direct dyes, which are suitable as single dye or in combination with other direct dyes, especially for semi permanent dyeing, are:

2-Amino-3-nitrophenol, 2-Amino-4-hydroxyethylamino-anisole sulfate, 2-Amino-6-chloro-4-nitrophenol, 2-Chloro-5-nitro-N-hydroxyethylene-p-phenyldiamine, 2-Hydroxyethyl-picramic acid, 2,6-Diamino-3-((pyridine-3yl)-azo)pyridine, 2-Nitro-5-glyceryl-methylaniline, 3-Methylamino-4-nitro-phenoxyethanol, 4-Amino-2-nitrodiphenyleneamine-2'-carboxylic acid, 6-Nitro-1,2,3,4,-tetrahydroquinoxaline, 4-N-Ethyl-1,4-bis(2'-hydroxyethylamino-2-nitrobenzene hydrochloride, 1-Methyl-3-nitro-4-(2'-hydroxyethyl)-aminobenzene, 3-Nitro-p-hydroxyethyl-aminophenol, 4-Amino-3-nitrophenol, 4-Hydroxypropylamine-3-nitrophenol (BN), Hydroxy-anthrylamino-propylmethyl morpholino methosulfat, 4-Nitrophenyl-aminoethylurea, 6-Nitro-p-toluidine, Acid Blue 62, Acid Blue 9, Acid Red 35, Acid Red 87 (Eosin), Acid Violet 43, Acid Yellow 1, Basic Blue 3, Basic Blue 6, Basic Blue 7, Basic Blue 9, Basic Blue 12, Basic Blue 26, Basic Blue 99, Basic Brown 16, Basic Brown 17, Basic Red 2, Basic Red 22, Basic Red 76, Basic Violet 14, Basic Yellow 57, Basic Yellow 9, Disperse Blue 3, Disperse Orange 3, Disperse Red 17, Disperse Violet 1, Disperse Violet 4, Disperse Black 9, Fast Green FCF, HC-Blue 2, HC-Blue 7, HC-Blue 8, HC-Blue 12, HC-Orange 1, HC-Orange 2, HC-Red 1, HC-Red 10-11, HC-Red 13, HC-Red 16, HC-Red 3, HC-Red BN, HC-Red 7, HC-Violet 1, HC-Violet 2, HC-Yellow 2, HC-Yellow 5, HC-Yellow 5, HC-Yellow 6, HC-Yellow 7, HC-Yellow 9, HC-Yellow 12, HC-Red 8, Hydroxyethyl-2-nitro-p-toluidine, N,N-Bis-(2-Hydroxyethyl)-2-nitro-p-phenyldiamine (BS), Picramic Acid, Solvent Green 7.

Also, cationic azo dyes, for example according to GB-A-2 319 776 as well as the oxazine dyes described in DE-A-299 12 327 and mixtures thereof with the other direct dyes mentioned therein, are likewise suitable for combination.

Preferred direct dyes, which are suitable as single dye or in combination with other direct dyes or oxidative dyes and oxidization agents, especially for semi permanent dyeing and permanent dyeing, are:

Disperse Violet 4, Picramic acid, N,N'-Bis-(2-Hydroxyethyl) -2-nitro-p-phenyldiamine, HC Yellow No. 5, HC Blue No. 2, HC Yellow No. 2, 2-Chloro-5-nitro-N-hydroxyethyl-p-phenyldiamine, HC Red No. 3, 4-Amino-3-nitrophenol, Basic Blue 99, 2-Hydroxyethyl Picramic acid, HC Yellow No. 6, Hydroxyethyl-2-nitro-p-toluidine, 2-Amino-6-chloro-4-nitrophenol, 4-Hydroxypropylamino-3-nitrophenol, Basic Red 2, HC Red No. 16 and HC Blue No. 16.

In the following suitable cationic dyes for the combination with the method according to the present invention are described.

Preferred cationic dyes are described

- in WO 95/01772, especially on page 2, line 7 to page 4, line 1, and especially on page 4, line 35 to page 8, line 21 and on pages 11 to 27, or
- in WO 01/66646, especially on page 1, line 18 to page 3, line 16, and preferred from page 16, line 20 to page 22, and cationic dyes as described on pages 10 to 17, or
- in EP 970 685, especially on page 2, line 44 to page 9, line 56 and preferably on page 9, line 58 to page 48, line 12, or
- direct dyes are described in DE-A-19 713 698, especially page 2, line 61 to page 3, line 43, or
- direct dyes and oxidizing agent are described in WO 97/20545, especially on page 1, lines 4 to 10, in particular on page 3, lines 24 to 32, and on page 11, line 6 to page 13, line 19, especially direct dyes are described on page 5, line 28 to page 8, line 20, or
- cationic dyes and anionic UV-absorbers are described in EP 1 166 752, especially on page 3, line 20 to page 4, line 21, in particular with UV absorber on page 4, lines 26 to 3, and especially on page 7, line 47 to page 9, line 56.

More preferred are cationic dyes as described in WO 01/66646, especially on page 16, example 1, and on page 19, example 4, or as described in WO 95/01772, especially on page 11, example 1, and on page 13, example 4, or as described in WO 01/11708, especially example 6, compound of formula 106.

Also very suitable for combination with the method according to the invention are cationic nitroaniline and anthraquinone dyes, for example those described in the following patent specifications: US-5 298 029, especially in column 2, line 33 to column 5, line 38; US-5 360 930, especially in column 2, line 38 to column 5, line 49; US-5 169 403, especially in column 2, line 30 to column 5, line 38; US-5 256 823, especially in column 4, line 23 to column 5, line 15; US-5 135 543, especially in column 4, line 24 to column 5, line 16; EP-A-818 193, especially on page 2, line 40 to page 3, line 26; US-5 486 629, especially in column 2, line 34 to column 5, line 29; and EP-A-758 547, especially on page 7, line 48 to page 8, line 19.

Also very suitable for combination with the method according to the invention are mixtures of cationic dyes with other dyes:

- mixtures of at least two cationic dyes as described in WO 95/01772, especially on page 8, line 34 to page 10, line 22 with the given preferences, or
- combinations of Pyrazolo-[1,5-a]-pyrimidines with at least one cationic dye as described in EP 998,908, especially on page 2, line 34 to line 42, with preferred Pyrazolo-[1,5-a]-pyrimidines as described in EP 998,908, especially on page 2, line 48 to page 4, line 3, and with preferred cationic direct dyes as described in EP 998,908, especially on page 4, line 22 to page 47, line 24, or
- combinations of cationic dyes as described in FR-2788432, especially on page 53, line 1 to page 63, line 23, especially a combination of cationic dyes with Arianors in FR-2788432, especially on pages 51 to 52, or especially a combination with at least one Basic Brown 17, Basic brown 16, Basic Red 76 and Basic Red 118, and/or at least one Basic Yellow 57, and/or at least one Basic Blue 99, or
- combinations of direct dyes and/or an oxidation dye and oxidizing agents in the form of permanent-wave fixing solution, especially with direct dyes as described in DE-A-19 713 698, especially page 4, line 65 to page 35, line 59, or

- combinations of cationic dyes and an oxidation dye of the developer compound type and oxidizing agents as described in EP 850 638, especially on page 2, line 27 to page 7, line 46 and preferred on page 7, line 20 to page 9, line 26, or
- combinations of an extemporaneous mixture of a composition (A) containing one or more oxidation dye precursors and optionally one or more couplers, and of a composition (B), in powder form, containing one or more direct dye, preferably cationic, optionally dispersed in an organic pulverulent excipient and/or a mineral pulverulent excipient, and a composition (C) containing one or more oxidizing agent as described in US 6,190,421, especially in column 2, lines 2 to 1, and preferably with oxidation dye precursors as described in column 2, line 35 to column 5, line 13, and preferably with direct dyes as described in column 5, line 30 to column 7, line 14, or
- a ready-to-use composition comprising, at least one oxidation base, at least one cationic direct dye and at least one enzyme of 2-electron oxidoreductase type in the presence of at least one donor for the said enzyme as described in US 6,228,129, especially in column 26, line 26 to column 27, line 9 with cationic direct dyes as described in column 8, line 17 to column 13, line 65, especially those as described in column 20, line 11 to line 19, in column 23, line 61 to column 24, line 25, or
- compositions of at least one direct cationic dye and at least one nitrated benzene dye as described in WO 99/20235 on page 2, line 1 to page 7, line 9, and on page 39, line 1 to page 40b line 11, with cationic direct dyes as described on page 8, line 12 to page 25 line 6, and nitro benzene direct dyes as described on page 26, line 7 to page 30, line 15, or
- compositions of at least one direct cationic dye and at least one autooxidisable oxidation dye, especially benzene, indol and indoline derivatives as described in WO 99/20234, with in preferred direct dyes as given on page 2, line 17 to page 26, line 4, and autooxidisable oxidation dye as described especially on page 26, line 10 to page 28, line 15, or
- oxidation dyeing compositions of at least one direct dye and at least one meta-Aminophenol derivative and at least one developer compound and an oxidizing agent as described in EP 850 636, especially on page 5, line 41 to page 7, line 52, and preferably on page 19, line 50 to page 22, line 12, with preferred direct dye as described on page 18, lines 1 and 2 in connection with page 7, line 53 to page 17, line 55, and with preferred meta-Aminophenol derivatives as described on page 7,

line 47 to line 52, and with preferred developer compounds as described on page 6, line 10 to page 7, line 46, or

- oxidation dyeing compositions of at least one direct dye and at least one developer compound selected from the group of para-Phenylenediamine derivatives and Bis-Phenylalkylenediamine and, and at least one coupler compound selected from the group of meta-Diphenols and an oxidizing agent, as described in EP-A-850 637, especially on page 6, line 50 to page 8, line 44,
- oxidation dyeing compositions with cationic couplers, as described in WO 99/48856, especially on page 9, line 16 to page 13, line 8, and page 11, line 20 to page 12, line 13, or
- cationic dye and e.g. a pyrazolo-(1,5-a)-pyrimidine derivatives, as described in EP 998 908, especially on page 2, line 34 to page 4, line 23, or
- arianoren and/or oxidative dyes, as described in FR-2 788 432, especially on page 2, line 16 to page 3, line 16, and page 5, line 19 to page 14, line 8, and combinations with cationic dyes as described on page 14, line 23 and following, or
- oxidative dye precursors (unsaturated aldehyde and coupler compounds), as described in German Patent Application 197 172 24, especially unsaturated aldehydes as described on page 2, line 50 to line 66 and page 3 line 8 to line 12 are used as developer compounds, and primary and secondary amino group compounds, nitrogen-containing heterocyclic compounds, amino acids, oligopeptids, aromatic hydroxy compounds, CH-active compounds as described on page 3, line 42 to page 5 line 25 are used as coupler compounds.

Also cationic azo dyes, e.g. according to GB-A-2 319 776, as well as the oxazine dyes described in DE-A-29 912 327 and mixtures thereof with the other direct dyes mentioned therein, can likewise readily be combined.

Especially preferred direct dye mixtures comprising a dye of formula (1) of WO 01/66646, and also the yellow dye according to Example 1 of WO 95/1772 and/or the red dye according to Example 4 of WO 95/1772 and/or the orange dye according to Example 46 of WO 95/1772.

No particular limitation is imposed on the acid dye used in the present invention so far as it is a water-soluble acid dye.

For the purpose of further modification of color shades, the method of colouring according to the invention may comprise customary acid dyes, for example from the group of the compounds known by the international names (Color index), or trade names.

Preferred examples of acid dyes are described in US Patent 6,248,314, they include Red Color No. 120, Yellow Color No. 4, Yellow Color No. 5, Red Color No. 201, Red Color No. 227, Orange Color No. 205, Brown Color No. 201, Red Color No. 502, Red Color No. 503, Red Color No. 504, Red Color No. 506, Orange Color No. 402, Yellow Color No. 402, Yellow Color No. 406, Yellow Color No. 407, Red Color No. 213, Red Color No. 214, Red Color No. 3, Red Color No. 104, Red Color No. 105(1), Red Color No. 106, Green Color No. 2, Green Color No. 3, Orange Color No. 207, Yellow Color No. 202(1), Yellow Color No. 202(2), Blue Color No. 202, Blue Color No. 203, Blue Color No. 205, Blue Color No. 2, Yellow Color No. 203, Blue Color No. 201, Green Color No. 201, Blue Color NO. 1, Red Color No. 230(1), Red Color No. 231, Red Color No. 232, Green Color No. 204, Green Color No. 205, Red Color No. 401, Yellow Color No. 403(1), Green Color No. 401, Green Color No. 402, Black Color No. 401 and Purple Color No. 401, especially Black Color No. 401, Purple Color 401, Orange Color No. 205.

These acid dyes may be used either single or in any combination thereof.

Preferably they are incorporated in a proportion of 0.001 - 5% by weight (hereinafter indicated merely by "%"), particularly 0.005 - 4%, more particularly 0.2 - 3% based on the total weight of the composition, from the viewpoint of practical use in that a sufficient hair-dyeing effect is achieved, and the hand skin is scarcely smeared.

Also very suitable for combination with the method according to the invention are uncharged dyes, for example from the group of the nitroanilines, nitrophenylenediamines, nitroaminophenols, anthraquinones, indophenols, phenazines, phenothiazines, bispyrazolons or bispyrazol aza derivatives or methines.

Also very suitable for combination with the method according to the invention are oxidation dyes.

Suitable oxidation dyes are described for example in

- German Patent Application 19 94 450, especially on page 6, line 6 to line 64, or
- German Patent Application 19 959 479, especially in column 2, line 6 to column 3, line 11, or
- in the series "Dermatology", edited by Ch. Culnan, H. Maibach, Verlag Marcel Dekker Inc., New York, Basle, 1986, Vol. 7, Ch. Zviak, The Science of Hair Care, chapter 8, on pages 264 - 267 (oxidation dyes), or
- in German Patent Application 19 717 224; unsaturated aldehydes as described on page 2, line 50 to line 66 and on page 3 line 8 to line 12 are used as developer compounds, and primary and secondary amino group compounds, nitrogen-containing heterocyclic compounds, amino acids, oligopeptides, aromatic hydroxy compounds, CH-active compounds as described on page 3, line 42 to page 5 line 8 are used as coupler compounds.

Oxidation dye precursors of the developer type are for example primary aromatic amines, which are substituted in the para- or ortho- position with a substituted or unsubstituted hydroxy- or amino residue, or diaminopyridine derivatives, heterocyclic hydrazones, 4-amino-pyrazol derivatives, 2,4,5,6-tetraaminopyrimidin derivatives, or unsaturated aldehydes as described in German Patent Application 19 717 224, especially on page 2, line 50 to line 66 and on page 3 line 8 to line 12, or cationic developer compounds as described in WO 00/43367, especially on page, 2 line 27 to page 8, line 24, in particular on page 9, line 22 to page 11, line 6.

Also very suitable for combination with the method according to the invention are developer dyes in their physiological compatible acid addition salt form, such as hydrochloride or sulfate. Developer dyes which have aromatic OH substituents are also suitable in their salt form with base, such as alkalimetalphenolates.

Preferred developer compounds are:

1,4-diamino-benzene (p-phenylenediamine), 1,4-diamino-2-methyl-benzene (p-toluylen-diamine), 1,4-diamino-2,6-dimethyl-benzene, 1,4-diamino-2,5-dimethyl-benzene, 1,4-

diamino-2,3-dimethyl-benzene, 2-chloro-1,4- diaminobenzene, 4-phenylamino-aniline, 4-di-methylamino-aniline, 4-diethylamino-aniline, hydroxyethyl-p-phenylendiamine, 1-(2'-hydroxyethyl)-2,5-diaminobenzene, N,N-bis-(2-hydroxyethyl)-p-phenylendiamine, 4-[(2-methoxyethyl)-amino]-aniline, 4-[(3-hydroxypropyl)amino]-aniline, hydroxypropyl-bis-(N-hydroxyethyl-p-phenylenediamine) hydrochloride, 1,4-diamino-2-(2-hydroxyethyl)-benzene, 1,4-diamino-2-(1-methylethyl)- benzene, 2-(2,5- diaminophenoxy)-ethanol, 1,3-bis[(4-aminophenyl)(2-hydroxyethyl)amino]-2-propanol, bis-(2-hydroxy-5-aminophenyl)-methane, 1,4-bis-(4-aminophenyl)-diazacycloheptane, 1,8-bis(2,5-diaminophenoxy)-3,6-dioxaoctan, 1,10-bis-(2,5-diaminophenyl)-1,4,7,10-tetraoxadecane, hydroxyethyl-3,4-methylenedioxyaniline, p-aminophenol, o-aminophenol, m-aminophenol, 2-amino-6-methyl-phenol, 4-methylaminophenol sulfate, 4-amino-m-cresol, 6-amino-m-cresol, 6-amino-m-cresol, 2-amino-4-hydroxyethylaminoanisole, 2-amino-5- methyl-phenol, 4-amino-3-methylphenol, 4-methylamino-phenol, 2-aminomethyl-4-aminophenol, 4-amino-2-[(2-hydroxyethyl)-amino]methyl-phenol, 4- amino-2-(2-hydroxyethoxy)-phenol, 4-amino-2-(methoxymethyl)-phenol, 4-amino-2-(2-hydroxyethyl)-phenol, 2-hydroxymethylamino-4-aminophenol, bis-(4-aminophenyl)amine, 4-amino-3-fluorphenol, 2-hydroxymethyl-4-aminophenol, 4-amino-2-(diethylamino)- methyl)-phenol, 5-amino-salicylsäure, 2,5-diamino-pyridine, 2-amino-3-hydroxy-pyridine, 2,6-dimethoxy-3,5-diamino-pyridine, 2,4,5,6-tetraaminopyrimidine, 2-hydroxy-4,5,6-triaminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine, 2,4-dihydroxy- 5,6-diaminopyrimidine, 2-dimethylamino-4,5,6-triaminopyrimidine, 2,5,6-triamino-4-(1H)-pyrimidone, further 4,5-diaminopyrazol derivatives as described in EP 0 740 741 or WO 94/08970, especially 4,5-diamino-1-(2-hydroxyethyl)-1H- pyrazol, 4,5-diamino-1-(1-methylethyl)-1H-pyrazol, 4,5-diamino-1-[(4-methylphenyl)methyl]-1H-pyrazol, 1-[(4-chlorophenyl)methyl]-4,5-diamino-1H-pyrazol, 4,5-diamino-1-methyl-1H-pyrazol.

More preferred developer dyes are p-phenylendiamine, p-toluyldiamine, p-aminophenol, m-aminophenol, o-aminophenol, N,N-bis-(2-hydroxyethyl)-p-phenylendiamine sulfate, 2-amino-4-hydroxyethylaminoanisole sulfate, hydroxyethyl-3,4-methylenedioxyaniline, 1-(2'-hydroxyethyl)-2,5-diaminobenzene, 2,6-dimethoxy-3,5-diamino-pyridine, hydroxypropyl-bis-(N-hydroxyethyl-p-phenylenediamine) hydrochloride, hydroxyethyl-p-phenylendiamine sulfate, 4-amino-3-methylphenol, 4-methylaminophenol sulfate, 2-aminomethyl-4-aminophenol, 4,5-diamino-1-(2-hydroxyethyl)-1H- pyrazol, 4-amino-m-cresol, 6-amino-m-



cresol, 5-amino-6-chloro-cresol, 2,4,5,6-tetraaminopyrimidine, 2-hydroxy-4,5,6-triaminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine sulfate.

Preferred oxidation dye precursors of the coupler type are for example m-phenylenediamine derivatives, naphthole, resorcinol and resorcinol derivatives, pyrazolone and m-aminophenol derivatives.

Especially preferred coupler compounds are N-(3-dimethylamino-phenyl)-urea, 4-amino-2-hydroxytoluene, 2-methyl-5-hydroxyethylaminophenol, 2,4-diaminophenoxyethanol, 2-amino-4-[(2-hydroxyethyl)amino]-anisole, p-aminophenol, m-aminophenol and its derivatives, especially 5-amino-2-methylphenol, 5-(3-hydroxypropylamino)-2-methylphenol, 3-amino-2-chloro-6-methylphenol, 2-hydroxy-4-aminophenoxyethanol, 2,6-dimethyl-3-aminophenol, 3-trifluoroacetyl-amino-2-chloro-6-methylphenol, 5-amino-4-chloro-2-methylphenol, 5-amino-4-methoxy-2-methylphenol, 5-(2'-hydroxyethyl)-amino-2-methylphenol, 3-(diethylamino)-phenol, N-cyclopentyl-3-aminophenol, 1,3-dihydroxy-5-(methylamino)-benzene, 3-(ethylamino)-4-methylphenol and 2,4-dichloro-3-aminophenol,

- o-aminophenol and its derivatives, such as 5-methyl-2-(1-methylamino)-phenol, 3-dimethylamino-phenol, 3-diethylamino-phenol, 5-amino-2-methyl-phenol, 5-amino-4-fluor-2-methyl-phenol, 5-amino-4-methoxy-2-methyl-phenol, 5-amino-4-ethoxy-2-methyl-phenol, 3-amino-2,4-dichlor-phenol, 5-amino-2,4-dichlor-phenol, 3-amino-2-methyl-phenol, 3-amino-2-chlor-6-methyl-phenol, 3-amino-phenol, 2-[(3-hydroxyphenyl)amino]-acetamide, 5-[(2-hydroxyethyl)amino]-2-methyl-phenol, 3-[(2-hydroxyethyl)amino]-phenol, 3-[(2-methoxyethyl)amino]-phenol, 5-amino-2-ethyl-phenol, 2-(4-amino-2-hydroxyphenoxy)-ethanol, 5-[(3-hydroxypropyl)amino]-2-methyl-phenol, 3-[(2,3-dihydroxypropyl)amino]-2-methyl-phenol, 3-[(2-hydroxyethyl)amino]-2-methyl-phenol,
- m-diaminobenzene and its derivatives such as 2,4-diaminophenoxyethanol, 1,3-bis-(2,4-diaminophenoxy)-propane, 1-methoxy-2-amino-4-(2'-hydroxyethylamino)-benzene, 1,3-bis-(2,4-diaminophenyl)-propane, 3-[(2-aminoethyl)amino]-aniline, 1,3-di-(2,4-diaminophenoxy)-propane, 1,3-diamino-2,4-dimethoxy-benzene, 2,6-bis(2-hydroxyethyl)amino-toluene, di(2,4-diaminophenoxy)-methane, 3-[di(2-hydroxyethyl-

- )amino]-aniline, 2,6-bis-(2-hydroxyethylamino)-1-methylbenzene and 1-amino-3-bis-(2'-hydroxyethyl)-aminobenzene,
- o-diaminobenzene and its derivatives such as 3,4-diaminobenzoic acid and 2,3-diamino-1-methylbenzene, 2,4-diamino-1-fluor-5-methyl- benzene, 2,4-diamino-1-methoxy-5-methyl-benzene, 1-(2-aminoethoxy)-2,4- diaminobenzene, 2-amino-1-(2-hydroxyethoxy)-4-methylamino-benzene, 2,4-diaminophenoxy-acetic acid, 2,4-diamino-1-ethoxy-5- methyl-benzene, 3-[(2-hydroxyethyl)amino]-aniline, 3,4-diaminobenzoic acid, 3,4-dihydro-6-hydroxy-1,4(2H)-benzoxazine, 6-amino-3,4-dihydro-1,4(2H)- benzoxazine, 2,4-diamino-1,5-di(2-hydroxyethoxy)-benzene, 2,4-diamino-1-(2-hydroxyethoxy)-5-methyl-benzene, 4-amino-2-di[(2-hydroxyethyl)amino]-1-ethoxybenzene 2,4-di[(2-hydroxyethyl)amino]-1,5-dimethoxy-benzene, 3,4-dihydro-6-hydroxy-1,4(2H)-benzoxazine, 6-amino-3,4-dihydro-1,4(2H)- benzoxazine,
  - di- or trihydroxybenzene derivatives such as resorcline, resorcinmonomethylether, 2-methylresorcline, 5-methylresorcline, 2,5-dimethylresorcline, 1-chloro-2,4-dihydroxybenzene, 2-chlororesorcline, 4-chlororesorcline, 2, 6-dihydroxyethylaminotoluene, 1,2-dichlor-3,5-dihydroxy-4-methyl-benzene, 1,5-dichlor-2,4-dihydroxy- benzene, 1,3-dihydroxy-2-methyl-benzene, pyrogallol and 1,2,4-trihydroxybenzene,
  - pyridine derivatives such as 2,6-diamino-pyridine, 2,6-dihydroxypyridine, 2-amino-3-hydroxypyridine, 2-amino-5-chloro-3-hydroxypyridine, 5-amino-4-chloro-2-methylphenol, 3-diamino-6- methoxy-pyridine, 3-amino-2-methylamino-6-methoxypyridine, 2,6- dihydroxy-3,4-dimethylpyridine, 2,6-dihydroxy-4-methylpyridine, 2,6-diaminopyridine, 2,3-diamino-6-methoxypyridine, 2,6-diamino-3,5-dimethoxy-pyridine, and 3,5-diamino-2,6-dimethoxypyridine,
  - naphthaline derivatives such as 1-naphthol, 2-methyl-1-naphthol, 2-hydroxymethyl-1-naphthol, 2-hydroxyethyl-1-naphthol, 1,5-dihydroxynaphthaline, 1,6-dihydroxynaphthaline, 1,7-dihydroxynaphthaline, 1,8-dihydroxynaphthaline, 2,7-dihydroxynaphthaline and 2,3-dihydroxynaphthaline, 2-methyl-1-naphthol-acetat,
  - morpholine derivatives such as 6-hydroxybenzomorpholine and 6-aminobenzo-morpholine,
  - chinoxaline derivatives such as 6-methyl-1,2,3,4-tetrahydrochinoxaline,
  - pyrazol derivatives such as -phenyl-3-methylpyrazol-5-one, 3-methyl-1-phenyl-5-pyrazolone,

- indol derivatives such as 4-hydroxyindol, 5-hydroxy-indol, 6-hydroxyindol and 7-hydroxyindol, 2,3-indolindione, 5,6-dihydroxy-indol, 5,6-dihydroxy-indoline,
- methylenedioxybenzene derivates such as 1-hydroxy-3,4-methylenedioxybenzene, 1-amino-3,4-methylenedioxybenzene and 1-(2'-hydroxyethyl)-amino-3,4-methylenedioxybenzene, 3,4-methylenedioxy-phenol, 3,4-methylenedioxy-aniline, 5-[(2-hydroxyethyl)amino]-1,3-benzodioxol, 6-brom-1-hydroxy-3,4-methylenedioxy-benzene, or
- cationic coupler compounds as described in FR 2 794 644, especially on page 11, line 20 to page 15, line 34, and on page 17, lines 4 to 12, page 178, line 33 to page 18, line 24.

More especially preferred coupler compounds are toluene-2,5-diamine sulfate, 1-naphthol, 1,5-, 2,7- and 1,7-dihydroxynaphthaline, 3-aminophenol, 5-amino-2-methylphenol, 2-amino-3-hydroxypyridine, resorcinol, 4-chlororesorcine, 2-chloro-6-methyl-3-aminophenol, 2,6-dihydroxyethylaminotoluene, 2-methyl-5-dihydroxyethylaminophenol, 2,4-diaminophenoxyethylol hydrochloride, 2-methylresorcine, 5-methylresorcine, 2,5-dimethylresorcine, 3,4-methylenedioxyphenol, 2-amino-4-hydroxyethylaminoanisole sulfate, 2,6-di-(beta -hydroxyethylamino)-toluene, 4-amino-2-hydroxytoluene, 6-hydroxyindol, 2-amino-3-hydroxypyridine, 2,6-dimethoxy-3,5-pyridinediamine hydrochloride and 2,6-dihydroxy-3,4-dimethylpyridine.

Most preferred coupler compounds are 2-chloro-6-methyl-3-aminophenol, 5-amino-2-methylphenol, 2-amino-3-hydroxypyridine, 2,6-di-(beta -hydroxyethylamino)-toluol, 2-methylresorcine and 1-naphthol.

The developer/-coupler combination 2,4,5,6-Tetraaminopyrimidine and 2-Methylresorcine are preferred for assessing of red shades, or  
 p-Toluenediamine and 4-Amino-2-hydroxytoluene are preferred for assessing of blue-violet shades, or  
 p-Toluenediamine and 2-Amino-4-hydroxyethylaminoanisole are preferred for assessing of blue shades, or  
 p-Toluenediamine and 2,4-Diamino-phenoxyethynol are preferred for assessing of blue shades, or  
 3-Methyl-4-aminophenol and 4-Amino-2-hydroxytoluene are preferred for assessing of orange shades, or

p-Toluenediamine and resorcline are preferred for assessing of brown-green shades, or p-Toluenediamine and 1-Naphthol are preferred for assessing of blue-violet shades, or p-Toluenediamine and 2-methylresorcline are preferred for assessing of brown-gold shades.

Further, the colouring method according to the present invention may also contain autooxidizable compounds, such as, for example benzene, indol, or indoline, especially 5,6-dihydroxyindol or 5,6-dihydroxyindoline derivatives as described in WO 99/20234, especially on page 26, line 10 to page 28, line 15, or in WO 00/28957 on page 2, third paragraph.

Preferred autooxidizable benzene derivatives are:

1,2,4-trihydroxybenzene, 1-methyl-2,4,5-trihydroxybenzene, 2,4-diamnio-6-methylphenol, 2-amino-4-methylaminophenol, 2,5-diamino-4-methyl-phenol, 2,6-diamino-4-diethylamino-phenol, 2,6-diamino-1,4-dihydroxybenzen, and the salts of these compounds, which are accessible with acid.

Preferred autooxidizable indol derivatives are:

5,6-dihydroxyindol, 2-methyl-5,6-dihydroxyindol, 3-methyl-5,6-dihydroxyindole, 1-methyl-5,6-dihydroxyindol, 2,3-dimethyl-5,6-dihydroxyindol, 5-methoxy-6-dihydroxyindol, 5-acetoxy-6-hydroixyindol, 5,6-diacetoxyindol, acid of 5,6-dihydroxyindol-2-carbonacid, and the salts of these compounds, which are accessible with acid.

Preferred autooxidizable indoline derivatives are:

5,6-dihydroxyindollne, 1-methyl-5,6-dihydroxyindoline, 1-ethyl-5,6-dihydroxyindoline, and the salts of these compounds, which are accessible with acid.

The colouring method according to the present invention also concerns the joint use of at least two different developers and at least one coupler compound, or combinations of at least two different couplers and at least one developer compound. Such combinations are for example described in German Patent Application 197 172 24, especially on page 3, line 31 to page 5, line 8.

In addition, the colouring method according to the present invention may also contain naturally occurring dyes, such as, for example, henna red, henna neutral, henna black, camomile blossom, sandalwood, black tea, Rhamnus frangula bark, sage, campeche wood,

madder root, catechu, sedre and alkanet root. Such colouring methods are described, for example, in EP-A-404 868, especially on page 3, line 55 to page 4, line 9.

One further embodiment of the present invention concerns formulations, which are used for the colouration of keratin fibres, especially human hair.

The formulations are applicable on human hair in different technical forms. The specific technical form may be chosen in view of the envisaged application and/or dye or dye composition. Technical forms of formulation are for example a solution, especially a thickened watery or watery alcoholic solution, a cream, foam, a gel, or an emulsion.

Preferred forms of formulations are ready to use compositions or a multi-compartment dyeing device or 'kit' or any of the multi-compartment packaging systems with compartments as described for example as described in US 6,190,421, column 2, lines 16 to 31.

The colouring compositions for carrying out the method according to the invention may furthermore comprise any active ingredient, additive or adjuvant known for such preparations.

Adjuvants that are suitable for such formulations are in general customary in the field hair-colouring, such as for example surfactants or tensides, solvents, bases, acids, perfumes, polymeric adjuvant, thickeners and light stabilisers.

Suitable combinations of the colouring compositions for carrying out the method according to the invention with adjuvant used in the colouring of hair, for example with

- combination of direct dyes with oxidizing agents to achieve lightened colouration; wherein oxidizing agents especially described in WO 97/20545, especially page 9, lines 5 to 9,
- combination of direct dyes and/or an oxidation dye and oxidizing agents in the form of permanent-wave fixing solution, especially oxidizing agents as described in DE-A-19 713 698 , especially page 4, lines 52 to 55, or EP-A-1 062 940, especially page 6, lines 41 to 47, (and in the equivalent WO 99/40895),
- oxidation dyes in the presence of oxidoreductase enzyme, as described in WO 99/17730, especially page 4, line 11 to page 13, line 28, and WO 99/36034, especially pages 3 to 15,

- combination of cationic dyes with polyols or polyethers; polyols or polyethers as described in EP-A-962 219, especially page 27, lines 14 to 38,
- thickening polymers, as described in EP-A-970 684, especially page 48, line 16 to page 51, line 4,
- sugar-containing polymers, as described in EP-A-970 687, especially page 28, line 17 to page 29, line 23,
- quaternary ammonium salts, as described in WO 00/10517, especially page 44, line 16 to page 46, line 23,
- anionic surfactants, as described in WO 00/10518, especially page 45, line 11 to page 48, line 3,
- non-ionic surfactants, as described in WO 00/10519, especially page 45, line 11 to page 50, line 12, or
- silicones, as described in WO 00/12057, especially page 45, line 9 to page 55, line 2.
- oxidative agent or laser and direct dyes, as described in EP-920 856, especially on page 2, line 31 to page 53 line 36, and on page 49, line 38 to page 50, line 41, with direct dyes as described on page 3, line 54 to page 48, line 52, or
- direct dyes in the presence of cationic amphotere, substantive polymer, as described in EP-953 334, especially on page 2, line 39 to page 7, line 44, with direct dyes as described on page 8, line 54 to page 27, line 16, and polymers as described on page 27, line 17 to page 30, line 14, or
- direct dyes formulations with polymer thickener on the basis of acrylic acid, as described in EP-970 685, especially on page 2, line 39 to page 10, line 1, with direct dyes as described on page 10, line 7 to page 48, line 15, with polymers as described on page 48, line 17 to page 49, line 28.

The colouring composition for carrying out the method according to the invention in many cases comprise at least one surfactant, there being suitable in principle anionic and also zwitterionic, ampholytic, non-ionic and cationic surfactants. In many cases, however, it has proved advantageous to select the surfactants from anionic, zwitterionic and non-ionic surfactants.

Anionic surfactants suitable for use in the colouring compositions for carrying out the method according to the invention include all anionic surface-active substances that are suitable for

use on the human body. Such substances are characterised by an anionic group that imparts water solubility, for example a carboxylate, sulfate, sulfonate or phosphate group, and a lipophilic alkyl group having approximately from 10 to 22 carbon atoms. In addition, glycol or polyglycol ether groups, ester, ether and amide groups and also hydroxy groups may be present in the molecule. The following are examples of suitable anionic surfactants, each in the form of sodium, potassium or ammonium salts or mono-, di- or tri-alkanolammonium salts having 2 or 3 carbon atoms in the alkanol group:

- linear fatty acids having from 10 to 22 carbon atoms (soaps),
- ether carboxylic acids of formula  $R-O-(CH_2-CH_2-O)_x-CH_2-COOH$ , in which R is a linear alkyl group having from 10 to 22 carbon atoms and  $x = 0$  or from 1 to 16,
- acyl sarcosides having from 10 to 18 carbon atoms in the acyl group,
- acyl taurides having from 10 to 18 carbon atoms in the acyl group,
- acyl isothionates having from 10 to 18 carbon atoms in the acyl group,
- sulfosuccinic mono- and di-alkyl esters having from 8 to 18 carbon atoms in the alkyl group and sulfosuccinic monoalkylpolyoxyethyl esters having from 8 to 18 carbon atoms in the alkyl group and from 1 to 6 oxyethyl groups,
- linear alkane sulfonates having from 12 to 18 carbon atoms,
- linear  $\alpha$ -olefin sulfonates having from 12 to 18 carbon atoms,
- $\alpha$ -sulfo fatty acid methyl esters of fatty acids having from 12 to 18 carbon atoms,
- alkyl sulfates and alkyl polyglycol ether sulfates of formula  $R'-O-(CH_2-CH_2-O)_x-SO_3H$ , in which  $R'$  is a preferably linear alkyl group having from 10 to 18 carbon atoms and  $x' = 0$  or from 1 to 12,
- mixtures of surface-active hydroxysulfonates according to DE-A-3 725 030, especially page 3, lines 40 to 55,
- sulfated hydroxyalkylpolyethylene and/or hydroxyalkylenepropylene glycol ethers according to DE-A-3 723 354, especially page 4, lines 42 to 62,
- sulfonates of unsaturated fatty acids having from 12 to 24 carbon atoms and from 1 to 6 double bonds according to DE-A-3 926 344, especially page 2, lines 36 to 54,
- esters of tartaric acid and citric acid with alcohols which are addition products of

approximately from 2 to 15 molecules of ethylene oxide and/or propylene oxide with fatty alcohols having from 8 to 22 carbon atoms, or

- anionic surfactants, as described in WO 00/10518, especially page 45, line 11 to page 48, line 3.

Preferred anionic surfactants are alkyl sulfates, alkyl polyglycol ether sulfates and ether carboxylic acids having from 10 to 18 carbon atoms in the alkyl group and up to 12 glycol ether groups in the molecule, and also especially salts of saturated and especially unsaturated C<sub>8</sub>-C<sub>22</sub>carboxylic acids, such as oleic acid, stearic acid, isostearic acid and palmitic acid.

Surface-active compounds that carry at least one quaternary ammonium group and at least one -COO<sup>(-)</sup> or -SO<sub>3</sub><sup>(-)</sup> group in the molecule are termed zwitterionic surfactants. Zwitterionic surfactants that are especially suitable are the so-called betaines, such as the N-alkyl-N,N-dimethylammonium glycinate, for example cocoalkyldimethylammonium glycinate, N-acylaminoethyl-N,N-dimethylammonium glycinate, for example cocoacylaminoethyl-N,N-dimethylammonium glycinate, and 2-alkyl-3-carboxymethyl-3-hydroxyethylimidazolines having from 8 to 18 carbon atoms in the alkyl or acyl group and also cocoacylaminoethylhydroxyethylcarboxymethyl glycinate. A preferred zwitterionic surfactant is the fatty acid amide derivative known by the CTFA name cocoamidopropyl betaine.

Ampholytic surfactants are to be understood as meaning surface-active compounds that, in addition to a C<sub>8</sub>-C<sub>18</sub>-alkyl or -acyl group, contain at least one free amino group and at least one -COOH or -SO<sub>3</sub>H group in the molecule and are capable of forming internal salts. Examples of suitable ampholytic surfactants include N-alkylglycines, N-alkylpropionic acids, N-alkylaminobutyric acids, N-alkyliminodipropionic acids, N-hydroxyethyl-N-alkylamidopropylglycines, N-alkyltaurines, N-alkylsarcosines, 2-alkylaminopropionic acids and alkylaminoacetic acids, each having approximately from 8 to 18 carbon atoms in the alkyl group. Ampholytic surfactants to which special preference is given are N-cocoalkylaminopropionate, cocoacylaminoethylaminopropionate and C<sub>12</sub>-C<sub>18</sub>acylsarcosine.

Non-ionic surfactants are described in WO 00/10519, especially page 45, line 11 to page 50, line 12.



Non-ionic surfactants contain as the hydrophilic group, for example, a polyol group, a polyalkylene glycol ether group or a combination of polyol and polyglycol ether groups.

Such compounds are, for example:

- addition products of from 2 to 30 mol of ethylene oxide and/or from 0 to 5 mol of propylene oxide with linear fatty alcohols having from 8 to 22 carbon atoms, with fatty acids having from 12 to 22 carbon atoms and with alkylphenols having from 8 to 15 carbon atoms in the alkyl group,
- C<sub>12</sub>-C<sub>22</sub> fatty acid mono- and di-esters of addition products of from 1 to 30 mol of ethylene oxide with glycerol,
- C<sub>8</sub>-C<sub>22</sub>alkyl-mono- and -oligo-glycosides and ethoxylated analogues thereof,
- addition products of from 5 to 60 mol of ethylene oxide with castor oil and hydrogenated castor oil,
- addition products of ethylene oxide with sorbitan fatty acid esters,
- addition products of ethylene oxide with fatty acid alkanolamides.

Examples of cationic surfactants that can be used in the colouring compositions for carrying out the method according to the invention are especially quaternary ammonium compounds. Preference is given to ammonium halides, such as alkyltrimethylammonium chlorides, dialkyldimethylammonium chlorides and trialkylmethylammonium chlorides, for example cetyltrimethylammonium chloride, stearyltrimethylammonium chloride, distearyldimethylammonium chloride, lauryldimethylammonium chloride, lauryldimethylbenzylammonium chloride and tricetylmethylammonium chloride. Further cationic surfactants that can be used in accordance with the invention are quaternised protein hydrolysates.

- Also suitable in accordance with the invention are cationic silicone oils, such as, for example, the commercially available products Q2-7224 (manufacturer: Dow Corning; a stabilised trimethylsilylamodimethicone), Dow Corning 929 emulsion (comprising a hydroxylamino-modified silicone, which is also referred to as amodimethicone), SM-2059 (manufacturer: General Electric), SLM-55067 (manufacturer: Wacker) and also Abil®-Quat 3270 and 3272 (manufacturer: Th. Goldschmidt; diquaternary polydimethylsiloxanes, quaternium-80), or silicones, as described in WO 00/12057, especially page 45, line 9 to page 55, line 2.

Alkylamidoamines, especially fatty acid amidoamines, such as the stearylamidopropyl-dimethylamine obtainable under the name Tego Amid® 18, are distinguished not only by a good conditioning action but also especially by their good biodegradability.

Quaternary ester compounds, so-called "esterquats", such as the methyl hydroxyalkyl-dialkoyloxyalkylammonium methosulfates marketed under the trademark Stepanex®, are also very readily biodegradable.

An example of a quaternary sugar derivative that can be used as cationic surfactant is the commercial product Glucquat®100, according to CTFA nomenclature a "lauryl methyl gluceth-10 hydroxypropyl dimonium chloride".

The alkyl-group-containing compounds used as surfactants may be single substances, but the use of natural raw materials of vegetable or animal origin is generally preferred in the preparation of such substances, with the result that the substance mixtures obtained have different alkyl chain lengths according to the particular starting material used.

The surfactants that are addition products of ethylene and/or propylene oxide with fatty alcohols or derivatives of such addition products may either be products having a "normal" homologue distribution or products having a restricted homologue distribution. "Normal" homologue distribution is to be understood as meaning mixtures of homologues obtained in the reaction of fatty alcohol and alkylene oxide using alkali metals, alkali metal hydroxides or alkali metal alcoholates as catalysts. Restricted homologue distributions, on the other hand, are obtained when, for example, hydrotalcites, alkali metal salts of ether carboxylic acids, alkali metal oxides, hydroxides or alcoholates are used as catalysts. The use of products having restricted homologue distribution may be preferred.

Examples of further active ingredients, adjuvants and additives are as follows:

- non-ionic polymers, for example vinylpyrrolidone/vinyl acrylate copolymers, polyvinylpyrrolidone and vinylpyrrolidone/vinyl acetate copolymers and polysiloxanes,
- cationic polymers, such as quaternised cellulose ethers, polysiloxanes having quaternary groups, dimethyldiallylammonium chloride polymers, copolymers of dimethyldiallyl-

ammonium chloride and acrylic acid, as available commercially under the name Merquat® 280 and the use of which in hair colouring is described, for example, in DE-A-4 421 031, especially page 2, lines 20 to 49, or EP-A-953 334, especially page 27, line 17 to page 30, line 11, acrylamide/dimethyldiallylammonium chloride copolymers, diethyl-sulfate-quaternised dimethylaminoethyl methacrylate/vinylpyrrolidone copolymers, vinylpyrrolidone/imidazolinium methochloride copolymers,

- quaternised polyvinyl alcohol,
- zwitterionic and amphoteric polymers, such as, for example, acrylamido-propyl-trimethylammonium chloride/acrylate copolymers and octylacrylamide/methyl methacrylate/tert-butylaminoethyl methacrylate/2-hydroxypropyl methacrylate copolymers,
- anionic polymers, such as, for example, polyacrylic acids, crosslinked polyacrylic acids, vinyl acetate/crotonic acid copolymers, vinylpyrrolidone/vinyl acrylate copolymers, vinyl acetate/butyl maleate/isobornyl acrylate copolymers, methyl vinyl ether/maleic anhydride copolymers and acrylic acid/ethyl acrylate/N-tert-butyl acrylamide terpolymers,
- thickeners, such as agar, guar gum, alginates, xanthan gum, gum arabic, karaya gum, locust bean flour, linseed gums, dextrans, cellulose derivatives, e.g. methyl cellulose, hydroxyalkyl cellulose and carboxymethyl cellulose, starch fractions and derivatives, such as amylose, amylopectin and dextrans, clays, e.g. bentonite or fully synthetic hydrocolloids such as, for example, polyvinyl alcohol,
- structuring agents, such as glucose and maleic acid,
- hair-conditioning compounds, such as phospholipids, for example soya lecithin, egg lecithin, and cephalins, silicone oils, and also conditioning compounds, for example such as those described in DE-A-19 729 080, especially page 2, lines 20 to 49, EP-A-834 303, especially page 2, line 18 to page 3, line 2, or EP-A-312 343, especially page 2, line 59 to page 3, line 11,
- protein hydrolysates, especially elastin, collagen, keratin, milk protein, soya protein and wheat protein hydrolysates, condensation products thereof with fatty acids and also quaternised protein hydrolysates,
- perfume oils, dimethyl isosorbitol and cyclodextrins,
- solubilisers, such as ethanol, isopropanol, ethylene glycol, propylene glycol, glycerol and diethylene glycol,
- anti-dandruff active ingredients, such as piroctones, olamines and zinc Omadine,
- further substances for adjusting the pH value,

- active ingredients such as panthenol, pantothenic acid, allantoin, pyrrolidonecarboxylic acids and salts thereof, plant extracts and vitamins,
- cholesterol,
- light stabilisers and UV absorbers, as described, for example, in EP-A-819 422, especially page 4, lines 34 to 37,
- consistency regulators, such as sugar esters, polyol esters or polyol alkyl ethers,
- fats and waxes, such as spermaceti, beeswax, montan wax, paraffins, fatty alcohols and fatty acid esters,
- fatty alkanolamides,
- polyethylene glycols and polypropylene glycols having a molecular weight of from 150 to 50 000, for example such as those described in EP-A-801 942, especially page 3, lines 44 to 55,
- complexing agents, such as EDTA, NTA and phosphonic acids,
- swelling and penetration substances, such as polyols and polyol ethers, as listed extensively, for example, in EP-A-962 219, especially page 27, lines 18 to 38, for example glycerol, propylene glycol, propylene glycol monoethyl ether, butyl glycol, benzyl alcohol, carbonates, hydrogen carbonates, guanidines, ureas and also primary, secondary and tertiary phosphates, imidazoles, tannins, pyrrole,
- opacifiers, such as latex,
- pearlising agents, such as ethylene glycol mono- and di-stearate,
- propellants, such as propane-butane mixtures, N<sub>2</sub>O, dimethyl ether, CO<sub>2</sub> and air, and also
- antioxidants,
- polyols or polyethers, as described in EP-A-962 219, especially page 27, lines 14 to 38,
- thickening polymers, as described in EP-A-970 684, especially page 48, line 16 to page 51, line 4,
- sugar-containing polymers, as described in EP-A-970 687, especially page 28, line 17 to page 29, line 23,
  - quaternary ammonium salts, as described in WO 00/10517, especially page 44, line 16 to page 46, line 23.

In the context of the present invention, oxidizing agents are understood to be any oxidizing agent customarily used for oxidative hair colouring, for example dilute hydrogen peroxide solutions, hydrogen peroxide emulsions or hydrogen peroxide gels, alkaline earth metal

peroxides, organic peroxides, such as urea peroxides, melamine peroxides, or alkalimetalbromat fixations are also applicable if a shading powder on the basis of semi-permanent, direct hair dyes is used.

Preferred oxidizing agent is hydrogen peroxide, preferred in about 2 to 30 % by weight, more preferred in 3 to 20% by weight, and most preferred in 6 to 12% by weight of the total weight of a watery composition such as a solution, dispersion, a gel or emulsion.

The watery composition can comprise all customary components, which are used for the different applications of oxidizing agent compositions as described in K. Schrader, "Grundlagen und Rezepturen der Kosmetika", 2. Aufl. (1989), page 832-840.

Further preferred oxidizing agents are

- oxidizing agents to achieve lightened colouration, as described in WO 97/20545, especially page 9, lines 5 to 9,
- oxidizing agents in the form of permanent-wave fixing solution, as described in DE-A-19 713 698 , especially page 4, lines 52 to 55, and lines 60 and 61 or EP-A-1 062 940, especially page 6, lines 41 to 47, (and in the equivalent WO 99/40895).

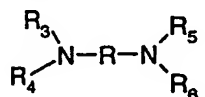
An oxidizing agents may be present in the colouring compositions for carrying out the method according to the invention preferably in an amount of from 0.01 % to 6 %, especially from 0.01 % to 1 %, based on the total dyeing composition.

Preferred catalysts are metal ions, such as for example  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Mn}^{4+}$ ,  $\text{Li}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Al}^{3+}$ , preferably  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Mn}^{2+}$ .

The metal ions are applicable in any physiological suitable salts form. Preferred salts are acetate, sulfate, halogenide, lactate and tartrate.

Alkalimetalsulfits, such as sodium-, potassium-, lithium-sulfite, Alkalimetaldisulfits, such as sodium-, potassium-, lithium-disulfite, ascorbic acid, tert.-Butylhydrochinon and Ammoniumthiolactat.

In general, the coloration with an oxidative agent is conducted in the presence of a base. Bases are for example ammonia, alkali metal carbonates, earth metal carbonates, alkanol amines, such as for example mono-, di- or triethanolamine, alkali metal hydroxides, earth metal hydroxides, compounds of the formula



wherein,

R is a propyl residue, which substituted with OH or C<sub>1</sub>-C<sub>4</sub>-alkyl,

R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub> and R<sub>6</sub> are independently or dependently from each other hydrogen, C<sub>1</sub>-C<sub>4</sub>-alkyl or hydroxy-(C<sub>1</sub>-C<sub>4</sub>)-alkyl.

Alkali metal is for example sodium, potassium or lithium.

Earth metal is for example magnesium or calcium.

Acids are inorganic or organic acids, such as hydrochloride, tartrat acid, citric acid, ascorbine acid and phosphor acid.

The use of UV absorbers can effectively protect natural and dyed hair from the damaging rays of the sun and increase the wash fastness of dyed hair.

Suitable UV absorbers the colouring compositions for carrying out the method according to the invention are:

- cationic benzotriazole UV absorbers as for example described in WO 01/36396 especially on page 1, line 20 to page 2, line 24, and preferred on page 3 to 5, and on pages 26 to 37, or
- cationic benzotriazole UV in combination with antioxidants as described in WO 01/36396, especially on page 11, line 14 to page 18, or
- UV absorbers in combination with antioxidants as described in US Patent 5 922 310, especially in column 2, lines 1 to 3,
- UV absorbers in combination with antioxidants as described in US Patent 4 786 493, especially in column 1, 42 to column 2, line 7, and preferred in column 3, 43 to column 5, line 20, or

- 50 -

- combination of UV absorbers as described in US Patent 5 830 441, especially in column 4, lines 53 to 56, or
- combination of UV absorbers as described in WO 01/36396, especially on page 11, lines 9 to 13, or
- triazine derivatives provide effective UV protection as described in WO 98/22447, especially on page 1, line 23 to page 2, line 4, and preferred on page 2, line 11 to page 3, line 15 and most preferred on pages 6 to 7, and 12 to 16, or
- combination of the cosmetic formulations as described in WO 98/22447 with one or more than one further UV filter as described in the following patents:

(Abbreviations T: table, R: row, Comp: compound, Ex: compound(s) of patent example, p: page)

EP 895776	Comp. in Rows 48-58, p 3; R 25+33, p 5
WO 9220690	Polymeric comp in Examples 3-6
EP 1000950	Comp. in Table 1, pp 18-21
EP 1060734	T 1-3, pp 11-14
EP 1059082	Ex 1; T 1, pp 9-11
EP 1008586	Ex 1-3, pp 13-15
EP 1005855	T 3, p 13
EP 1129695	Ex 1-7, pp 13-14
EP 967200	Ex 2; T 3-5, pp 17-20
EP 945125	T 3 a+b, pp 14-15
EP 924246	T 2, p 9
EP 911020	T 2, p 11-12
EP 916335	T 2-4, pp 19-41
EP 852137	T 2, pp 41-46
EP 858318	T 1, p 6
EP 826361	T 1, pp 5-6
EP 503338	T 1, pp 9-10
WO 9301164	T 1+2, pp 13-22
EP 823418	Ex 1-4, pp 7-8
WO 9714680	Ex 1-3, p 10
EP 1027883	Compound VII, p 3
EP 832641	Ex 5+6 p 7; t 2, p 8

US 5338539	Ex 1-9, pp 3+4
EP 517103	Ex 3,4,9,10 pp 6-7
EP 1123934	T 3, p 10
EP 1027883	Comp I-VI, p 3
EP 969004	Ex 5, T 1, pp 6-8
US 5801244	Ex 1-5, pp 6-7
EP 832642	Ex 22, T 3 pp, 10-15; T 4, p 16
US 5346691 (EP 570838)	Ex 40, p 7; T 5, p 8
EP 517104	Ex 1, T 1, pp 4-5; Ex 8, T 2, pp 6-8
WO 200149686	Ex 1-5, pp 16-21
EP 944624	Ex 1+2, pp13-15
EP 933376	Ex 1-15, pp 10-21
EP 863145	Ex 1-11, pp 12-18
EP 780382	Ex 1-11, pp 5-7
EP 626950	
EP 1081140	Ex 1-9, pp 11-16
WO 9217461	Ex 1-22, pp 10-20
WO 0168047	Tables on pp 85-96
EP 613893	Ex 1-5 + 15, T 1, pp 6-8
EP 1064922	Compounds 1-34, pp 6-14
EP 1028120	Ex 1-5, pp 5-13
EP 1008593	Ex 1-8, pp 4-5
EP 669323	Ex 1-3, p 5
EP 1108712	4,5-Dimorpholino-3-hydroxypyridazine
JP 2000319629	CAS Regno. 80142-49-0, 137215-83-9, 307947-82-6
EP 420707 B1	Ex 3, p 13 (80142-49-0)
US 5635343	
EP 1167358	

In addition to the triazine UV absorbers described in WO 98/22447, the cosmetic formulations can also contain one or more than one further UV protective of the following substance classes:



- p-aminobenzoic acid derivatives, for example 4-dimethylaminobenzoic acid 2-ethylhexyl ester;
- salicylic acid derivatives, for example salicylic acid 2-ethylhexyl ester;
- benzophenone derivatives, for example 2-hydroxy-4-methoxybenzophenone and its 5-sulfonic acid derivative;
- dibenzoylmethane derivatives, for example 1-(4-tert-butylphenyl)-3-(4-methoxyphenyl)-propane-1,3-dione;
- diphenylacrylates, for example 2-ethylhexyl 2-cyano-3,3-diphenylacrylate, and 3-(benzofuranyl) 2-cyanoacrylate;
- 3-imidazol-4-ylacrylic acid and esters;
- benzofuran derivatives, especially 2-(p-aminophenyl)benzofuran derivatives, described in EP-A-582 189, US-A-5 338 539, US-A-5 518 713 and EP-A-613 893;
- polymeric UV absorbers, for example the benzylidene malonate derivatives described in EP-A-709 080;
- cinnamic acid derivatives, for example the 4-methoxycinnamic acid 2-ethylhexyl ester and isoamyl ester or cinnamic acid derivatives described in US-A-5 601 811 and WO 97/00851;
- camphor derivatives, for example 3-(4'-methyl)benzylidene-bornan-2-one, 3-benzylidenebornan-2-one, N-[2(and 4)-2-oxyborn-3-ylidene-methyl]-benzyl]acrylamide polymer, 3-(4'-trimethylammonium)-benzylidene-bornan-2-one methyl sulfate, 3,3'-(1,4-phenylenedimethine)-bis(7,7-dimethyl-2-oxo-bicyclo[2.2.1]heptane-1-methanesulfonic acid) and salts, 3-(4'-sulfo)benzylidene-bornan-2-one and salts; camphorbenzalkonium methosulfate;
- hydroxyphenyltriazine compounds, for example 2-(4'-methoxyphenyl)-4,6-bis(2'-hydroxy-4'-n-octyloxyphenyl)-1,3,5-triazine; 2,4-bis[[4-(3-(2-propyloxy)-2-hydroxy-propyloxy)-2-hydroxy]-phenyl]-6-(4-methoxyphenyl)-1,3,5-triazine; 2,4-bis[[4-(2-ethylhexyloxy)-2-hydroxy]-phenyl]-6-[4-(2-methoxyethyl-carboxyl)-phenylamino]-1,3,5-triazine; 2,4-bis[[4-(tris(trimethylsilyloxy)-silylpropyloxy)-2-hydroxy]-phenyl]-6-(4-methoxyphenyl)-1,3,5-triazine; 2,4-bis[[4-(2"-methylpropenyloxy)-2-hydroxy]-phenyl]-6-(4-methoxyphenyl)-1,3,5-triazine; 2,4-bis[[4-(1',1',1',3',5',5',5'-heptamethyltrisilyl-2"-methyl-propyloxy)-2-hydroxy]-phenyl]-6-(4-methoxyphenyl)-1,3,5-triazine; 2,4-bis[[4-(3-(2-propyloxy)-2-hydroxy-propyloxy)-2-hydroxy]-phenyl]-6-[4-ethylcarboxy]-phenylamino]-1,3,5-triazine;



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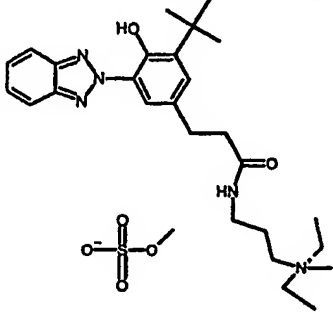
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UV	40	Triethanolamine salicylate	2174-16-5												
UV	41	3, 3'- (1, 4- phenylene-dimethylene)bis[7, 7-dimethyl- 2- oxo-bicyclo[2.2.1]heptane-1- methanesulfonic acid]	90457-82-2												
UV	42	Titanium dioxido	13463-67-7	5	7.5					25				10	10
UV	44	Zinc oxide	1314-13-2			15				10					10
UV	45	2,2'-Methylene-bis-[6-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethyl-butyl)-phenol]	103597-45-1				15		20	20				10	10
UV	46	2,4-bis[[4-(2-ethyl-hexyloxy)-2-hydroxy]-phenyl]-6-(4-methoxy-phenyl)-(1,3,5)-triazine	187393-00-6	10	15		15	15							10
UV	47	1H-Benzimidazole-4,6-disulfonic acid, 2,2'-(1,4-phenylene)bis-, disodium salt	180898-37-7					15							10
UV	48	Benzoic acid, 4,4'-[[6-[[4-[(1,1-dimethyl-ethyl)amino]carbonyl]-phenyl]amino]1,3,5-triazine-2,4-diyl]diimino]bis-, bis(2-ethylhexyl)ester	154702-15-5	20			15							10	10
UV	49	Phenol, 2-(2H-benzotriazol-2-yl)-4-methyl-6-[2-methyl-3-[1,3,3,3-tetramethyl-1-[(trimethylsilyl)oxy]-	155633-54-8			15					15			10	10

[illegible]

UV	55	1H-Benzimidazole-4,6-disulfonic acid, 2,2'-(1,4-phenylene)bis-	170864-82-1			15		10						10	10
UV	56	1,3,5-Triazine, 2,4,6-tris(4-methoxyphenyl)-	7753-12-0	10	7.5	15	10	5	50	25	25	25	10	10	10
UV	57	1,3,5-Triazine, 2,4,6-tris[4-[(2-ethylhexyl)oxy]phenyl]-	208114-14-1		15	10									10
UV	58	1-Propanaminium, 3-[[3-[3-(2H-benzotriazol-2-yl)-5-(1,1-dimethylethyl)-4-hydroxyphenyl]-1-oxopropyl]amino]-N,N-diethyl-N-methyl-, methyl sulfate (salt)	340964-15-0												
UV	59	2-Propenoic acid, 3-(1H-imidazol-4-yl)-	104-98-3												
UV	60	Benzoic acid, 2-hydroxy-, [4-(1-methylethyl)phenyl]methyl ester	94134-93-7												
UV	61	1,2,3-Propanetriol, 1-(4-aminobenzoate)	136-44-7												
UV	62	Benzeneacetic acid, 3,4-dimethoxy-a-oxo-	4732-70-1												
UV	63	2-Propenoic acid, 2-cyano-3,3-diphenyl-, ethyl ester	5232-99-5												

The following examples C1-C12 illustrate combinations of UV absorbers and antioxidants in cosmetic preparations which are useful to protect hair and natural or artificial hair color (% by weight, based on the total weight of the composition).

Compound (CAS No.)	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
	2	3	4	1	2	3	1	2	2.5	1
Benzenesulfonic acid, 3-(2H-benzotriazol-2-yl)-4-hydroxy-5-(1-methylpropyl)-, monosodium salt (92484-48-5)	1	1								
Propyl gallate (121-79-9)	1	0.5					1			1
N-[3-(3,5-Di-tert-butyl-4-hydroxyphenyl)propionyl] sulfanilic acid (or salts e.g. with sodium)			2	1				1	2	
Benzylidene malonate polysiloxane (207574-74-1)		2			0.2					
Drometrizole trisiloxane (155633-54-8)		1					0.5			
Diethylhexy Triazone (154702-15-5)				0.2						
Phenol, 2,2'-[6-(4-methoxyphenyl)-1,3,5-triazine-2,4-diyl]bis[5-[(2-ethylhexyl)oxy]- (187393-00-6)				0.2						
1H-Benzimidazole-4,6-disulfonic acid, 2,2'-(1,4-phenylene)bis-, disodium salt (180898-37-7)				1						
Bis-Benzotriazolyl Tetramethylbutyl-phenol (103597-45-1)					0.5					





Preference is given to the use of mixing ratios of triazine derivatives of formula 1-8/further light-protective agents from 1:99 to 99:1, especially from 1:95 to 95:1 and preferably from 10:90 to 90:10, based on weight. Of special interest are mixing ratios of from 20:80 to 80:20, especially from 40:60 to 60:40 and preferably approximately 50:50. Such mixtures can be used, *inter alia*, to improve solubility or increase UV absorption.

Synergistic effects are observed when UV absorbers are used in combination with antioxidants. Examples of antioxidants that can be used are listed in WO 01/36396 (pages 11-18), US Patent 5 922 310 and US Patent 4 786 493.

Examples of UV absorbers used in addition to the uncharged and cationic benzotriazole UV absorbers in the formulations without limitation to those listed in the following might be benzophenone-type substances such as benzophenone-1, benzophenone-2, benzophenone-3, benzophenone-4, benzophenone-5 (sodium salt) or benzotriazol-type substances such as benzenesulfonic acid, 3-(2H-benzotriazol-2-yl)-4-hydroxy-5-(1-methylpropyl)-, monosodium salt; 2-(5-chloro-2H-benzotriazol-2-yl)-6-(1,1-dimethylethyl)-4-methyl-phenol; 2-(2H-benzotriazol-2-yl)-6-dodecyl-4-methyl-phenol, branched and linear. Typical ingredients in the oil phase of emulsions (water in oil, oil in water or triple emulsion) or used in hair oils can be chosen from the following substance groups without limiting the kind of lipophilic ingredients to those substances:

Suitable cosmetic preparations may contain usually from 0.05 to 40 % by weight, preferably from 0.1 to 20 % by weight, based on the total weight of the composition, of one or more UV absorbers.

Preferred are the cosmetic preparations contain at least one triazine derivative UV absorber, for example, from 0.1 to 40 % by weight, preferably from 0.1 to 20 % by weight and especially from 0.5 to 10 % by weight, based on the total weight of the composition, and the cosmetic preparations contain at least one cationic benzotriazole from 0.05-20% by weight, preferred from 0.1-20% by weight, based on the total weight of the composition. Typical cosmetic formulations containing uncharged and/or cationic benzotriazoles and/or antioxidants alone or in combinations are rinse-off products (e.g. shampoos, hair rinses, conditioners etc.),

Suitable cosmetic formulations are:

- cosmetic hair-treatment preparations, e.g. hair-washing preparations in the form of shampoos and conditioners, hair-care preparations, e.g. pre-treatment preparations or leave-on products such as sprays, creams, gels, lotions, mousses and oils, or hair tonics, styling creams, styling gels, pomades, hair rinses, treatment packs, intensive hair treatments, hair-structuring preparations, e.g. hair-waving preparations for permanent waves (hot wave, mild wave, cold wave), hair-straightening preparations, liquid hair-setting preparations, hair foams, hairsprays, bleaching preparations, e.g. hydrogen peroxide solutions, lightening shampoos, bleaching creams, bleaching powders, bleaching pastes or oils, temporary, semi-permanent or permanent hair colourants, preparations containing self-oxidising dyes, or natural hair colourants, such as henna or camomile.

The final formulations listed may exist in a wide variety of presentation forms, for example:

- in the form of liquid preparations as a W/O, O/W, O/W/O, W/O/W or PIT emulsion and all kinds of microemulsions,
- in the form of a gel,
- in the form of an oil, a cream, milk or lotion,
- in the form of a powder, a lacquer, a tablet or make-up,
- in the form of a stick,
- in the form of a spray (spray with propellant gas or pump-action spray) or an aerosol,
- in the form of a foam, or
- in the form of a paste.

Of special importance as cosmetic preparations for the hair are the above-mentioned preparations for hair treatment, especially hair-washing preparations in the form of shampoos, hair conditioners, hair-care preparations, e.g. pre-treatment preparations, hair tonics, styling creams, styling gels, pomades, hair rinses, treatment packs, intensive hair treatments, hair-straightening preparations, liquid hair-setting preparations, hair foams and hairsprays. Of special interest are hair-washing preparations in the form of shampoos.

A shampoo has, for example, the following composition: from 0.01 to 5 % by weight of a UV absorber according to the invention, 12.0 % by weight of sodium laureth-2-sulfate, 4.0 % by weight of cocoamidopropyl betaine, 3.0 % by weight of sodium chloride, and water ad 100%.

Any known process suitable for the preparation of microparticles can be used for the preparation of the micronised UV absorbers, for example:

- wet-grinding with a hard grinding medium, for example zirconium silicate and a protective surfactant or a protective polymer in water or in a suitable organic solvent;
- spray-drying from a suitable solvent, for example aqueous suspensions or suspensions containing organic solvents, or true solutions in water, ethanol, dichloroethane, toluene or N-methylpyrrolidone etc.;
- by the expansion according to the RESS process (Rapid Expansion of Supercritical Solutions) of supercritical fluids (e.g. CO<sub>2</sub>) in which the UV filter or filters is/are dissolved, or the expansion of fluid carbon dioxide together with a solution of one or more UV filters in a suitable organic solvent;
- by reprecipitation from suitable solvents, including supercritical fluids (GASR process = Gas Anti-Solvent Recrystallisation / PCA process = Precipitation with Compressed Anti-solvents).

As grinding apparatus for the preparation of the micronised organic UV absorbers there may be used, for example, a jet mill, ball mill, vibratory mill or hammer mill, preferably a high-speed mixing mill. The grinding is preferably carried out with a grinding aid, for example an alkylated vinylpyrrolidone polymer, a vinylpyrrolidone/vinyl acetate copolymer, an acyl glutamate, an alkyl polyglucoside, cetareth-25 or a phospholipid.

The micronised UV absorbers so obtained usually have an average particle size that is from 0.02 to 2 µm, preferably from 0.05 to 1.5 µm, and more especially from 0.1 to 1.0 µm.

The UV absorbers can also be used dry in powder form. For that purpose the UV absorbers are subjected to known grinding methods, such as vacuum atomization, countercurrent spray-drying etc. Such powders have a particle size of from 0.1 µm to 2µm. To avoid the occurrence of agglomeration, the UV absorbers can be coated with a surface-active compound prior to the pulverisation process, for example with an anionic, non-ionic or amphoteric surfactant, e.g. a phospholipid or a known polymer, such as PVP, or an acrylate. The colouring compositions for carrying out the method according to the invention may further comprise antimicrobial agents.

Typical antimicrobial preservatives and antimicrobial actives used in formulations (in most cases the INCI name of the antimicrobial substances is mentioned):

formaldehyde and paraformaldehyde, hydroxy biphenyls and its salts such as ortho-phenylphenol, zinc pyrithion, chlorobutanol, hydroxy benzoic acids and their salts and esters such as methyl paraben, ethyl paraben, propyl paraben, butyl paraben, dibromo hexamidine and its salts including isothionate (4,4'-hexamethylenedioxy-bis(3-bromo-benzamidine) and 4,4'-hexamethylenedioxy-bis(3-bromo-benzamidinium 2-hydroxyethanesulfonate), mercury, (aceto-O)phenyl (especially phenyl mercuric acetate) and Mercurate(2-), (orthoborate(3-)-O)phenyl, dihydrogene (especially phenyl mercuric borate), 1,3-bis(2-ethylhexyl)-hexahydro-5-methyl-5-pyrimidine (Hexetidin), 5-bromo-5-nitro-1,3-dioxan, 2-bromo-2-nitro-1,3-propandiol, 2,4-dichlorobenzyl alcohol, 3,4,4' trichlorocarbanilide (Trichlorcarban), p-chloro-m-cresol, 2,4,4'-trichloro 2-hydroxy diphenylether (triclosan), 4,4'-dichloro 2-hydroxy diphenylether, 4-chloro-3,5-dimethylphenol (Chloroxylenol), imidazolidinyl urea, poly-(hexamethylene biguanide) hydrochloride, 2-phenoxy ethanol (phenoxyethanol), hexamethylene tetramine (Methenamine), 1-(3-chloroallyl)-3,5,7-triaza-1-azonia-adamantanchloride (Quaternium 15), 1-(4-chlorophenoxy)-1-(1-imidazolyl)3,3-dimethyl-2-butanone (Climbazole), 1,3-bis(hydroxymethyl)-5,5-dimethyl-2,4-imidazolidinedione (DMDM hydantoin), benzyl alcohol, 1,2-dibromo-2,4-dicyano butane, 2,2' methylene-bis(6-bromo-4-chloro phenol) (bromochlorophene), methylchlorisothiazolone, methylisothiazolone, octylisothiazolone, benzylisothiazolone, 2-benzyl-4-chlorophenol (Chlorophenone), chloracetamide, chlorhexidine, chlorhexidine acetate, chlorhexidine gluconate, chlorhexidine hydrochloride, 1-phenoxy-propane-2-ol (phenoxyisopropanol), 4,4-dimethyl-1,3-oxazolidine (dimethyl oxazolidine), diazolidinyl urea, 4,4'-hexamethylenedioxybisbenzamidine and 4,4'-hexamethylenedioxybis(benzamidinium-2-hydroxyethanesulfonate), glutaraldehyde (1,5-pentanedial), 7-ethylbicyclooxazolidine, 3-(4-chlorophenoxy)-1,2-propandiol (chlorophenesin), phenylmethoxymethanol and ((phenylmethoxy)methoxy)-methanol (benzylhemiformal), N-alkyl(C12-C22)trimethyl ammoniumbromide and -chloride (cetrimonium bromide, cetrimonium chloride), benzyl-dimethyl-(4-(2-(4-(1,1,3,3-tetramethylbutyl)-phenoxy)-ethoxy)-ethyl)-ammoniumchloride (benzethonium chloride), Alkyl-(C8-C18)-dimethyl-benzylammonium chloride, - bromide and saccharinate (benzalkonium chloride, benzalkonium bromide, benzalkonium saccharinate), benzoic acid and its salts and esters, propionic acid and its salts, salicylic acid and its salt, sorbic acid and its salts, sodium iodate, inorganic sulfites and bisulfites such as sodium sulfite, dehydroacetic acid, formic

acid, mercurate(1-ethyl)2-mercaptobenzoate(2-)-O,S-,hydrogene (Thiomersal or Thiomerosal), 10-undecylenic acid and its salts, octopirox (piroctone olamine), sodium hydroxy methyl-aminoacetate (sodium hydroxymethylglycinate), 3-iodo-2-propynyl butylcarbamate, 10-undecylenic acid, sulfur.

Combinations with natural antimicrobials or chemically modified natural substances with antimicrobial activities such as chitosans and chitosan derivatives, farnesol, plant extracts such as clove oil, blue cypres oil etc. can be also used.

For use on human hair, the dyeing compositions can usually be incorporated into an aqueous cosmetic carrier. Suitable aqueous cosmetic carriers include, for example, creams, sprays, emulsions, gels, powders and also surfactant-containing foaming solutions, e.g. shampoos or other preparations, that are suitable for use on keratin-containing fibers. Such forms of use are described in detail in Research Disclosure 42448 (August 1999). If necessary, it is also possible to incorporate the dyeing compositions into anhydrous carriers, as described, for example, in US-3 369 970, especially column 1, line 70 to column 3, line 55. The dyeing compositions according to the invention are also excellently suitable for the colouring method described in DE-A-3 829 870 using a colouring comb or a colouring brush.

Further carriers for dying compositions are for example described in "Dermatology", edited by Ch. Culnan, H. Maibach, Verlag Marcel Dekker Inc., New York, Basle, 1986, Vol. 7, Ch. Zviak, The Science of Hair Care, chapter 7, pages 248-250, especially on page 243, line 1 to page 244, line 12.

Suitable formulations of cationic dyes, which can be used in the colouring compositions for carrying out the method according to the invention are described for example in

- in WO 95/01772, especially on page 11, line 29 to page 12, line 7, or
- in WO 01/66646, especially on page 7, line 1 to page 22, and preferred from page 16, line 20 to page 22, or
- direct dyes as described in DE-A-19 713 698, especially page 3, line 51 to page 4, line 29 and page 4, line 65 to page 5, line 60, or
- direct dyes and oxidizing agent as described in WO 97/20545, especially on page 9, line 1 to page 11, line 4, in particular on page 11, line 6 to page 13, line 19.

Preferred formulations of cationic dyes with other dyes, which can be used in the colouring compositions for carrying out the method according to the invention, are:

- combinations of Pyrazolo-[1,5-a]-pyrimidines with at least one cationic dye as described in EP 998,908, especially on page 47, line 3 to page 49, line 26, and preferred on page 51, line 4 to page 52, line 5, or
- combinations of cationic dyes as described in FR-2788432, especially on page 53, line 1 to page 63, line 23, especially a combination of cationic dyes with Arianors in FR-2788432, especially on pages 51 to 52, or especially a combination with at least one Basic Brown 17, Basic brown 16, Basic Red 76 and Basic Red 118, and/or at least one Basic Yellow 57, and/or at least one Basic Blue 99, or
- combinations of direct dyes and/or an oxidation dye and oxidizing agents in the form of permanent-wave fixing solution, especially with direct dyes as described in DE-A-19 713 698 , especially page 4, line 65 to page 35, line 59, or
- combinations of cationic dyes and an oxidation dye of the developer compound type and oxidizing agents as described in EP 850 638, especially on page 2, lines 3 to 12 and line 30 to page 14, and page 28, line 35 to page 30, line 20, preferred on page 30, line 25 to page 32, line 30, or
- ready-to-use dyeing compositions and multicompartiment device for dyeing keratin fibers comprising combinations of an extemporaneous mixture of a composition (A) containing one or more oxidation dye precursors and optionally one or more couplers, and of a composition (B), in powder form, containing one or more direct dye, preferably cationic, optionally dispersed in an organic pulverulent excipient and/or a mineral pulverulent excipient, and a composition (C) containing one or more oxidizing agent as described in US 6,190,421, especially in column 2, line 20 to line 31 in column 7, line 15 to column 8, line 43, and preferably in column 8, line 55 to column 9, line 56, and preferably with direct dyes as described in column 5, line 30 to column 7, line 14, or
- a ready-to-use composition comprising, at least one oxidation base, at least one cationic direct dye and at least one enzyme of 2-electron oxidoreductase type in the presence of at least one donor for the said enzyme as described in US 6,228,129, especially in column 2, line 16 to column 25, line 55, and a multi-compartment dyeing device as described in column 26, lines 13 to 24, especially in column 26, line 26 to column 27, line 9, or

- a ready-to-use composition comprising compositions of at least one direct cationic dye and at least one nitrated benzene dye as described in WO 99/20235 especially on page 1, line 25 to page 8, line 5, and on page 30, line 17 to page 34 line 25, with cationic direct dyes as described on page 8, line 12 to page 25 line 6, and a multi-compartment dyeing device as described on page 35, lines 21 to 27, especially on page 36, line 1 to page 37, or
- a ready-to-use composition or a multi-compartment dyeing device comprising compositions of at least one direct cationic dye and at least one autooxidisable oxidation dye, especially benzene, indol and indoline derivatives as described in WO 99/20234, especially on page 26, line 5 to page 32, line 18, or
- oxidation dyeing compositions of at least one direct dye and at least one meta-Aminophenol derivative and at least one developer compound and an oxidizing agent as described in EP 850 636, especially on page 18, line 1 to page 22, line 11, or
- oxidation dyeing compositions of at least one direct dye and at least one developer compound selected from the group of para-Phenylenediamine derivatives and Bis-Phenylalkylenediamine and, and at least one coupler compound selected from the group of meta-Diphenols and an oxidizing agent, as described in EP-A-850 637, especially on page 19, line 24 to page 22, line 57,
- cationic dye and e.g. a pyrazolo-(1,5-a)-pyrimidine derivatives, as described in EP 998 908, especially on page 47, line 25 to page 50, line 29, or
- oxidative dye precursors (unsaturated aldehyde and coupler compounds), as described in German Patent Application 197 172 24, especially on page 3, line 36 to page 9 line 64.

Cationic dyes may be present in the colouring compositions for carrying out the method according to the invention preferably in an amount of from 0.001 % to 5 %, especially from 0.01 % to 1 %, based on the total dyeing composition.

The pH value of the ready-to-use dyeing preparations is usually from 2 to 11, preferably from 5 to 10.

The constituents of the aqueous carrier are used in the colouring compositions for carrying out the method according to the invention in the amounts customary for that purpose; for



example emulsifiers may be used in concentrations of from 0.5 to 30 % by weight and thickeners in concentrations of from 0.1 to 25 % by weight of the total dyeing composition.

If direct dyes are used together with oxidation dyes, they may be stored separately or together.

It is preferred to store the oxidation dyes and direct dyes, which are not stable to reduction, separate

They may be stored in a liquid to paste-like preparation (aqueous or non-aqueous) or in the form of a dry powder.

When the dyes and adjuvants are stored together in a liquid preparation, the preparation should be substantially anhydrous in order to reduce reaction of the compounds.

When they are stored separately, the reactive components are intimately mixed with one another only immediately before use. In the case of dry storage, before use a defined amount of hot (from 50 to 80°C) water is usually added and a homogeneous mixture prepared.

One preferred method of applying direct dyes containing formulations on hair is by using a multi-compartment dyeing device or "kit" or any other multi-compartment packaging system, as described for example in WO 97/20545 on page 4, line 19 to line 27.

The colouring compositions for carrying out the method according to the invention may combined with a suitable ready-to-use composition for the oxidation dyeing of keratin fibers, in particular human keratin, comprising an oxidizing agent, at least one direct dye and at least one oxidation dye precursor, as described in US 6,190,421, in column 1, line 65 to column 3, line 65, especially in column 10, line 62 to column 12, line 65.

Preferably, such a ready-to-use composition is prepared according to a first preferred embodiment by a process which comprises a preliminary step which involves separately storing, on the one hand, a composition (A) comprising, in a medium which is suitable for dyeing, at least one developer compound, especially selected from para-phenylenediamines

and bis(phenyl)alkylenediamines, and the acid-addition salts thereof, at least one coupler, especially selected from meta-phenylenediamines and the acid-addition salts thereof, and at least one cationic direct dye, on the other hand, a composition (B) containing, in a medium which is suitable for dyeing, at least one oxidizing agent and mixing them together at the time of use before applying this mixture to the keratin fibers.

According to a second preferred embodiment for the preparation of the ready-to-use dye composition, the process includes a preliminary step which involves separately storing, on the one hand, a composition (A) comprising, in a medium which is suitable for dyeing, at least one developer compound, especially selected from para-phenylenediamines and bis(phenyl)alkylenediamines, and the acid-addition salts thereof, at least one coupler compound, especially selected from meta-phenylenediamines and the acid-addition salts thereof; on the other hand, a composition (A') comprising, in a medium which is suitable for dyeing, at least one cationic direct dye and, lastly, a composition (B) containing, in a medium which is suitable for dyeing, at least one oxidizing agent as defined above, and mixing them together at the time of use before applying this mixture to the keratin fibers.

The composition (A') used according to this second variant of the process in accordance with the invention can optionally be in powder form, the cationic direct dye(s) in accordance with the invention itself (themselves) constituting, in this case, all of the said composition (A') or optionally being dispersed in an organic and/or inorganic pulverulent excipient.

When it is present in the composition A', the organic excipient can be of synthetic or plant origin and is selected in particular from crosslinked and non-crosslinked synthetic polymers, polysaccharides such as celluloses and modified or unmodified starches, as well as natural products containing them such as sawdust and plant gums (guar gum, carob gum, xanthan gum, etc.).

When it is present in the composition (A'), the inorganic excipient can contain metal oxides such as titanium oxides, aluminium oxides, kaolin, talc, silicates, mica and silicas.

An very suitable excipient in the colouring compositions for carrying out the method according to the invention is sawdust.

The powdered composition (A') can also contain binders or coating products in an amount which preferably does not exceed approximately 3% by weight relative to the total weight of the said composition (A').

These binders are preferably selected from oils and liquid fatty substances of inorganic, synthetic, animal or plant origin.

The composition (A') may optionally also contain other adjuvants, in powdered form, in particular surfactants of any kind, hair conditioners such as, for example, cationic polymers, etc.

Another subject of the invention is a multi-compartment dyeing device or "kit" or any other multi-compartment packaging system, as described for example in US 6,228,129, especially in column 26, lines 13 to 24, especially in column 26, line 26 to column 27, line 9, or. A first compartment which contains the composition (A) as defined above, an optional second compartment contains the composition (A') as defined above, when it is present, and a third compartment contains the oxidizing composition (B) as defined above. These devices can be equipped with means which allow the desired mixture to be applied to the hair, such as the devices described in French patent FR-2,586,913, the disclosure of which is specifically incorporated by reference herein.

An oxidizing agent, which may be added to the colouring compositions for carrying out the method according to the invention containing composition, comprises an oxidizing agent and a base.

Further, this composition comprises for this oxidizing agent containing composition customary adjuvant and additives.

The formulations are for example a solution, especially a thickened watery or watery alcoholic solution, a cream, foam, a gel, a powder or an emulsion.

In general, preference is given to a cream formulation, a gel formulation or a foam formulation, and especially a foam formulation.

But, if stability- or solubility- problems arise it may of advantage to use powder formulation as for example described in DE 197 13 698, page 2, line 26 to 54 and page 3, line 51 to page 4, line 25, and page 4, line 41 to page 5 line 59.

The oxidizing agent (calculated as hydrogen peroxide) is present in this composition in 0.5 to 12% by weight, in particular from 1 to 6% by weight based on the totals weight of the oxidizing agent containing composition.

The pH-value of the oxidizing agent containing composition is usually about 2 to 7, and in particular about 3 to 6.

An oxidizing agent free composition, which may be added to the colouring compositions for carrying out the method according to the invention, comprises a developer compound and a coupler compound and a reduction agent, or  
a developer compound or/and optionally a reduction agent, or  
a coupler compound and a reduction agent.

Further, an oxidizing agent free composition may additionally comprise a direct dye as for example described in German Patent Application 199 59 479, column 3, line 12 to line 16.

Additionally, the oxidizing agent free composition usually comprises customary adjuvant and additives. Preferred are those, which are described in German Patent Application, in column 3, line 17 to line 41.

The pH-value of the oxidizing agent free composition is usually about 3 to 11, and in particular about 5 to 10, and most particular about 9 to 10.

For adjusting the pH-value organic or inorganic acids, as for example described in German Patent Application 199 59 479, column 3, line 46 to line 53 are suitable.

The colouring compositions for carrying out the method according to the invention may also be combined with hair dye compositions comprising an acid dye. Hair dye compositions comprising an acid dye are known. For example, they are described in "Dermatology", edited by Ch. Culnan, H. Maibach, Verlag Marcel Dekker Inc., New York, Basle, 1986, Vol. 7,

Ch. Zviak, The Science of Hair Care, chapter 7, pages 248-250, especially on page 253 and 254.

The hair dye compositions comprising an acid dye have a pH of 2-6, preferably 2-5, more preferably 2.5-4.0. If the pH is too low, the resulting composition may roughen the hair, scalp and hand skin due to an acid component in some cases. If the pH is too high, the penetration accelerating effect on the acid dye is lowered.

The colouring method according to the present invention may also readily be used in combination with other dyes and/or adjuvants used in the colouring of hair, for example

- acid dye and an alkylene carbonate, as described in US patent 6,248,314, especially in examples 1 and 2, or
- acid hair dye compositions comprise various kinds of organic solvents represented by benzyl alcohol as a penetrant solvent have good penetrability into hair, as described in Japanese Patent Application Laid-Open Nos. 210023/1986 and 101841/1995, or
- acid hair dye compositions with a water-soluble polymer or the like to prevent the drooping of the hair dye composition, as described for example in Japanese Patent Application Laid-Open Nos. 87450/1998, 255540/1997 and 245348/1996, or
- acid hair dye compositions with a water-soluble polymer of aromatic alcohols, lower alkylene carbonates, or the like as described in Japanese Patent Application Laid-Open No. 53970/1998 and Japanese Patent Publication No. 23911/1973.

Preferred keratin fibers are human hair.

The dyes or dye precursors are suitable for all-over colouring of the hair, that is to say when colouring the hair on a first occasion, and also for re-colouring subsequently, or colouration of locks or parts of the hair.

The dyes or dye precursors are applied to hair for example through massage in by hand, a comb, a brush, or a bottle, or a bottle, which is combined with a comb or a nozzle.

In general, the dyes or dye precursors are applied to the hair in a formulation with further components, like adjuvants or additional dyes or dye precursors.

After the application of the dyeing composition the dyed hair is customary rinsed. Customary, the rinsing is conducted with water.

In a suitable embodiment of the processes of the present invention for dyeing human hair, the dyeing composition is not rinsed off, but washed off with a commercially available hair shampoo.

In general, the dyed hair is dried after rinsing and/or washing.

Customary, drying is conducted with hot air by means of a drier or the like, since color migration to clothes and the like becomes scarcely caused.

In the context of the present invention, the expression "a further dye", denotes preferably an oxidation dye, a diazotised compound, a capped diazotised compound and/or coupler compound, or acid dye, especially selected a cationic, anionic or uncharged direct dye.

A very suitable process for dyeing keratin fibers comprise contacting the keratin fibers under alkaline conditions with at least one capped diazotized compound and a coupler compound, with the proviso that the pH is adjusted in the range from 2 to 6 in the last process step. Adjusting the pH is achieved in conventional manner by adding an acid as described for example in EP 962218, especially on page 3, lines 12 to 16.

Acids are for example tartaric acid or citric acid, a citric acid gel, a suitable buffer solution with optionally an acid dye.

Preferred technical forms of acids are a solution, a gel, a cream, a foam, a conditioner, a emulsion, a shampoo and more preferred a shampoo or a conditioner.

In the context of the present invention, the expression "alkaline condition", denotes to all process steps without those wherein acid conditions are explicitly described.

In general, all processes for dyeing keratin fibers, in particular human hair, comprise after contacting the keratin fiber with a dye

- a) leaving the fibers to stand, and

b) then rinsing the fibers.

The process for dyeing keratin fibers, in particular human hair, with direct dyes comprises

a) contacting the keratin fibers with a direct dye.

The process for dyeing is for example described in WO 01/66646 on page 15, line 32 to page 16, line 2.

Usually, the dyeing compositions are usually applied to the hair in an amount of from 50 to 100 g.

This composition is left on the fiber at 15 to 45°C for 5 to 30 minutes, and in particular for 10 to 20 minutes at 20 to 30°C.

The method of colouring according to the invention in combination with at least one direct dye may further concerns a process for dyeing keratin fibres comprises

a) contacting the keratin fibers with at least one direct dye, a base and an oxidizing agent.

Compositions comprising at least one direct dye and an oxidizing agent, are for example described in WO 97/20545, on page 3, line 24 to page 11, line 4, and especially on page 4, line 9 to 17.

The composition comprising at least one direct dye, a base and an oxidizing agent is prepared by mixing at least one direct dye and a base, and then just before the dyeing of the hair, adding an oxidizing agent.

Alternatively, the oxidizing agent can be applied simultaneously with a composition comprising at least one dye and a base.

Preferably, the process for dyeing keratin fibres with at least one direct dye comprises using a multi-compartment dyeing device or 'kits' as described for example in WO 97/20545, especially on page 4, line 19 to line 27.

Suitable processes for enlightening dyeing, which can be used in combination with the method for colouring according to the invention are described in WO 97/20545, on page 11 to page 13.

Suitable processes for dyeing with cationic dyes, which can be combined with the method of colouring according to the present invention, are described

- in WO 95/01772, especially on page 10, line 24 to page 11, line 16, and especially on page 11, line 29 to page 28, or
- in WO 01/66646, especially on page 1, line 18 to page 3, line 16, and preferred from page 16, line 20 to page 22, or
- in EP 970 685, especially on page 50, lines 15 to 43, and preferred from page 50, line 46 to page 51, line 40, or
- in DE-A-19 713 698 , especially page 5, lines 26 to 60, or
- a process of dyeing with direct dyes and oxidizing agent is described in WO 97/20545, especially on page 10, line 10 to page 11, line 55 and preferably on page 11, line 6 to page 13, line 19.

Suitable processes for dyeing with combinations of cationic dyes and other dyes, which can be combined with the method of colouring according to the present invention, are:

- mixtures of at least two cationic dyes as described in WO 95/01772, especially on page 11, lines 1 to 15, or
- combinations of Pyrazolo-[1,5-a]-pyrimidines with at least one cationic dye as described in EP 998,908, especially on page 50, lines 15 to 28, or
- combinations of cationic dyes as described in FR-2788432, especially on page 49, line 28 to page 52, and preferred on page 50, lines 16 to 28, or
- combinations of direct dyes and/or an oxidation dye and oxidizing agents in the form of permanent-wave fixing solution, especially with direct dyes as described in DE-A-19 713 698 , especially on page 2, lines 12 to 23, especially on page 4, line 65 to page 5, line 59, or
- combinations of cationic dyes and an oxidation dye of the developer compound type and oxidizing agents as described in EP 850 638, especially on page 29, line 42 to page 30, line 20 and preferred on page 30, line 25 to page 32, line 30, or



- combinations of an extemporaneous mixture of a composition (A) containing one or more oxidation dye precursors and optionally one or more couplers, and of a composition (B), in powder form, containing one or more direct dye, preferably cationic, optionally dispersed in an organic pulverulent excipient and/or a mineral pulverulent excipient, and a composition (C) containing one or more oxidizing agent as described in US 6,190,421, especially in column 8, lines 43 to 52, and preferably in column 8, line 55 to column 9, line 55, or
- a ready-to-use composition comprising, at least one oxidation base, at least one cationic direct dye and at least one enzyme of 2-electron oxidoreductase type in the presence of at least one donor for the said enzyme as described in US 6,228,129, especially in column 25, line 56 to column 27, line 9, or
- a ready-to-use composition or multi-compartment dyeing device comprising compositions of at least one direct cationic dye and at least one nitrated benzene dye as described in WO 99/20235 on page 34, line 27 to page 37, or
- a ready-to-use composition or multi-compartment dyeing device comprising compositions of at least one direct cationic dye and at least one autooxidisable oxidation dye, especially benzene, indol and indoline derivatives as described in WO 99/20234, especially on page 32, line 20 to page 35, oxidation dyeing compositions of at least one direct dye and at least one meta-Aminophenol derivative and at least one developer compound and an oxidizing agent as described in EP 850 636, especially on page 18, line 1 to page 22, line 11, or
- oxidation dyeing compositions of at least one direct dye and at least one developer compound selected from the group of para-Phenylenediamine derivatives and Bis-Phenylalkylenediamine and, and at least one coupler compound selected from the group of meta-Diphenols and an oxidizing agent, as described in EP-A-850 637, especially on page 19, line 24 to page 22, line 57,
- cationic dye and e.g. a pyrazolo-(1,5-a)-pyrimidine derivatives, as described in EP 998 908, especially on page 47, line 25 to page 50, line 29, or
- arianors and/or oxidative dyes, as described in FR-2 788 432, especially on page 2, line 16 to page 3, line 16, and page 5, line 19 to page 14, line 8, and combinations with cationic dyes as described on page 14, line 23 and following, or

- oxidative dye precursors (unsaturated aldehyde and coupler compounds), as described in German Patent Application 197 172 24, especially on page 3, line 36 to page 9 line 64.

The method of colouring of keratin fibers, especially human hair, according to the present invention may combined with direct dyes and oxidative dyes.

The process for dyeing keratin fibers with direct dyes and oxidative dyes, in particular human hair, comprises

- a) contacting the keratin fibers with an oxidizing agent, optionally containing at least a direct dye,
  - b) then contacting the keratin fibers with an oxidizing agent free composition, optionally containing at least a direct dye,
- or
- a) contacting the keratin fibers with an oxidizing agent free composition, optionally containing at least a direct dye,
  - b) then contacting the keratin fibers with an oxidizing agent, optionally containing at least a direct dye.

The method of colouring according to the present invention may combined with a process for dyeing keratin fibers with direct dyes and oxidative dyes, which comprises

- a) contacting the keratin fibers with at least one direct dye,
- b) then contacting the keratin fibers with an oxidizing agent free composition.

Such process is for example described in DE 199 41 450, especially on page 5, lines 50 to 58, and on page 8, line 31 to 46.

Oxidizing agent is usually applied in form of an oxidizing agent containing composition. Oxidizing agent free composition containing at least one coupler compound, at least one developer compound, a base and a reduction agent.

Customary, the oxidizing agent containing composition is evenly applied in a sufficient amount related to the amount of hair, usually with 30 to 200 g.

In general, the oxidizing agent containing composition is left on the fiber at 15 to 45°C for 0 to 15 minutes, and in particular for 0 to 5 minutes.

Then the oxidizing agent free composition is applied to the hair.

In general, the direct dye and oxidizing agent free composition is left on the fiber at 15 to 50°C for 5 to 45 minutes, and in particular for 10 to 25 minutes.

The coupler and developer compounds of the oxidizing agent free composition can be applied simultaneously or in succession. Preferred is a simultaneous application.

One preferred embodiment of the process is to wash the hair with shampoo and or a weak acid, such as citric acid or tartrate acid.

The direct dyes, which are stable to reduction can stored together with the oxidizing agent free compositions and are applicable as composition.

It is of advantage to prepare compositions of direct dyes, which are not stable to reduction, with oxidizing agent free compositions just before the dyeing process.

Further, a direct dye and an oxidizing agent free composition can be applied simultaneously or in succession.

A suitable process for the coloration of keratin fiber with direct dyes and oxidation dyes, which can be used in combination with the method of colouring according to the present invention, comprises

- a) mixing at least one direct dye and optionally at least one coupler compound and at least one developer compound, and an oxidizing agent, which optionally contains at least one direct dye, and
- b) then contacting the keratin fibers with the mixture as prepared in step a).

A further suitable process for the coloration of keratin fiber with direct dyes and oxidation dyes, which can be used in combination with the method of colouring according to the present invention, comprises

- a) mixing at least one autooxidable compound and at least one developer compound and at least one direct dye, and
- b) then contacting the keratin fibers with the mixture prepared in step a).

The direct dye is usually applied in form of a composition, comprising further adjuvants, in particular an aqueous composition.

In general the mixing is conducted just before contacting the keratin fibers.

Usually, the mixture prepared in process step a) is evenly applied in a sufficient amount related to the amount of hair, usually with 30 to 200 g.

In general, the mixture is left on the fiber at 15 to 45°C for 0 to 50 minutes, and in particular for 30 to 45 minutes.

One preferred embodiment of the processes is to wash the hair with shampoo and or a weak acid, such as citric acid or tartrate acid, as for example described in EP 962218, especially on page 3, lines 9 to 18.

One suitable embodiment of the present invention concerns in addition to the method according to the present invention, the separate application of a direct dye and an oxidation dye is for example as described in DE-A-19 713 698, especially page 4, line 65 to page 35, line 59, wherein the keratin fibres are contacted in a first step with a direct dye, especially in form of a tinting powder, and an oxidizing agent, and then, in a second step, with an oxidizing free composition, especially in form of a powder.

Further, it is possible to apply for example a ready-to-use composition for the oxidation dyeing of keratin fibers, in particular human keratin fibers such as hair, as described in US 6,190,421, in column 1, line 65 to column 3, line 65, especially in column 10, line 62 to column 12, line 65.

According to this process, the ready-to-use dye composition as defined above is applied to the fibers and is left on them for an exposure time preferably of from approximately 3 to

approximately 40 minutes, more preferably from approximately 5 to approximately 30 minutes, after which the fibers are rinsed, optionally washed with shampoo, rinsed again and dried.

If unsaturated aldehydes are used as oxidative precursor dye together with a coupler compound no oxidizing agent is needed as described in German Patent Application 19 717 224.5. Nevertheless, it may be desirable to conduct the colouring in the presence of oxidizing agents, if lightening or a unified colouration of the keratin fiber is envisaged.

The process of dyeing keratin fibers with oxidative dye precursors, which can be used in combination with the method of colouring according to the present invention, comprises

- a) contacting the keratin fibers with an unsaturated aldehyde, a coupler compound and a direct dye.

In all above-cited dyeing processes it is also possible to apply a mixture of coupler compounds /and or developer compounds and/ different direct dyes.

Another preferred embodiment of the processes for oxidative dyeing of keratin fibers, which can be used in combination with the method of colouring according to the present invention, comprise applying to the keratin fibers after contacting with an oxidizing agent free composition containing a coupler compound and a developer compound and optionally a direct dye with a further oxidizing agent free composition containing a coupler compound and a developer compound and optionally an oxidizing agent containing composition and optionally a direct dye by a pH range from 5 to 7, preferred from 6.5 to 7. In general the keratin fiber is not washed or rinsed afterwards as for example described in EP 962217, especially on page 3, lines 9 to 17.

The developer and coupler compounds can be applied separately, simultaneously or in succession.

In all above-cited dyeing processes with oxidation dye precursors it is also possible to apply a mixture of coupler compounds /and or developer compounds.

A more suitable process for the dyeing of keratin fibers with oxidative dyes, which can be used in combination with the method of colouring according to the present invention, comprises,

- a) contacting the keratin fibers with an oxidizing agent containing composition,
- b) then contacting the keratin fibers with an oxidizing agent free composition.

Such process is for example described in DE 19959479, especially in column 3, line 54 to column 4, line 8.

Usually, the oxidizing agent containing composition is evenly applied in a sufficient amount related to the amount of hair, usually with 30 to 200 g.

In general, the oxidizing agent containing composition is left on the fiber at 15 to 50°C for 0 to 15 minutes, and in particular for 0 to 30 minutes.

Then the oxidizing agent free composition is applied.

Customary, the oxidizing agent free composition is left on the fiber at 15 to 50°C for 5 to 45 minutes, and in particular for 10 to 25 minutes.

The coupler and developer compounds of oxidizing agent free compositions can be applied as an admixture, or separately simultaneously or in succession. Preferred is the application of an admixture.

One suitable embodiment of the processes is to wash the hair with shampoo and or a weak acid, such as citric acid or tartrate acid, as for example described in EP 962218, especially on page 3, lines 9 to 18.

A further suitable process for the coloration of keratin fiber with oxidation dyes, which can be used in combination with the method of colouring according to the present invention, comprises

- a) mixing at least one coupler compound and developer compound, and an oxidizing agent, and
- b) then contacting the keratin fibers with the mixture as prepared in step a).

A further suitable process for the coloration of keratin fiber with an oxidation dye, which can be used in combination with the method of colouring according to the present invention, comprises

- a) mixing an autooxidable compound and a developer compound, and
- b) then contacting the keratin fibers with the mixture prepared in step a).

Especially preferred is a process for dyeing keratin fibers, in particular human hair, with capped diazotised compounds, which comprises,

- a) contacting the keratin fibers, under alkaline conditions, with at least one capped diazotised compound and a coupler compound, and optionally an oxidising agent, and optionally in the presence of a further dye,
- b) then adjusting the pH in the range of 6 to 2 by treatment with acid, optionally in the presence of a further dye.

The capped diazotised compound and coupler compound and optionally the oxidizing agent, can be applied in any desired order successively, or simultaneously.

Preferably, however, the capped diazotised compound and the coupler compound are applied simultaneously, in a single composition.

Customary the dyeing composition is applied to the hair in an amount of from 50 to 100 g.

In the context of the present invention, the expression "alkaline conditions" denotes a pH in the range from 8 to 10, preferably 9-10, especially 9.5-10.

Adding bases, for example sodium carbonate, ammonia or sodium hydroxide, to the hair or to the dye precursors, the capped diazotised compound and/or the water-soluble coupling component, or to colouring compositions comprising the dye precursors, customarily achieve the alkaline conditions.

In the second stage, the diazotised compound and the coupler compound are then caused to react, preferably by lowering the pH to a value of from 6 to 2, especially from 3 to 4.

A preferred embodiment of all processes of the present invention for dyeing keratin fibers comprise contacting the keratin fibers under alkaline conditions with at least one capped

diazotized compound and a coupler compound, with the proviso that the pH is adjusted in the range from 2 to 6 in the last process step.

Adjusting the pH is achieved in conventional manner by adding an acid as described for example in EP 962218, especially on page 3, lines 12 to 16.

Acids are for example tartaric acid or citric acid, a citric acid gel, a suitable buffer solution with optionally an acid dye.

Preferred technical forms of acids are a solution, a gel, a cream, a foam, a conditioner, a emulsion, a shampoo and more preferred a shampoo or a conditioner.

The ratio of the amount of alkaline colouring composition applied in the first stage to that of acid colouring composition applied in the second stage is preferably about from 1:3 to 3:1, especially about 1:1.

This first alkaline and then acid dyeing compositions each are left on the fiber at 15 to 45°C for 5 to 60 minutes, and in particular for 5 to 45 minutes at 20 to 30°C.

In the methods according to the invention, whether or not colouring is to be carried out in the presence of a further dye will depend upon the colour shade to be obtained.

In the context of the present invention, the expression "a further dye", denotes preferably an oxidation dye, a diazotised compound, a capped diazotised compound and/or coupler compound, or acid dye, especially selected a cationic, anionic or uncharged direct dye, especially a cationic dye selected from the group of the cationic dyes as described in WO 95/01772, especially on page 2, line 7 to page 4, line 1, and preferred on page 4, line 35 to page 8, line 21 with the given preferences, and as described in WO 01/66646, especially on page 1, line 18 to page 3, line 16, or a mixture of at least two cationic dyes as described in WO 95/01772, especially on page 8, line 34 to page 10, line 22.

A preferred embodiment of the process for dyeing keratin fibres with capped diazotised compounds and a coupler compound, comprises contacting the keratin fibres with more than one capped diazotised compound and/or more than one coupler compound.



Preferred is a process of the present invention for the coloration of keratin fiber with capped diazotised compounds comprises

- a) mixing, under alkaline conditions, at least one with capped diazotised compound and at least one coupler compound and at least one direct dye and optionally at least one developer compound; and an oxidizing agent, which optionally contains at least one direct dye, and
- b) then contacting the keratin fibers with the mixture as prepared in step a),
- c) then adjusting the pH in the range of 6 to 2 by treatment with acid, optionally in the presence of a further dye.

More preferred is a process for dyeing keratin fibres with at least one capped diazotized compound, which comprises

- a) mixing under alkaline conditions, at least one capped diazotized compound and at least one direct dye, a base and an oxidizing agent, and
- b) then contacting the keratin fibers with the mixture as prepared in step a),
- c) then adjusting the pH in the range of 6 to 2 by treatment with acid, optionally in the presence of a further dye.

Further, preferred is a process for the coloration of keratin fiber with capped diazotised compounds comprising

- a) mixing under alkaline conditions, at least one with capped diazotised compound and at least one coupler compound and optionally at least one direct dye and optionally at least one developer compound, and optionally at least one autooxidable compound, and
- b) then contacting the keratin fibers with the mixture prepared in step a),
- c) then adjusting the pH in the range of 6 to 2 by treatment with acid, optionally in the presence of a further dye.

A further suitable process for the two-step direct dyeing of keratin fibres, which can be used in combination with the method of colouring according to the present invention, is characterized in that,

- a) contacting the keratin fibers with an oxidizing agent or an oxidizing agent containing composition,

- b) then contacting the keratin fibers with at least one capped diazotised compound and at least a coupler compound and optionally a direct dye or/and optionally an oxidizing agent free composition,
- c) then adjusting the pH in the range of 6 to 2 by treatment with acid, optionally in the presence of a further dye.

or

- a) contacting the keratin fibers with at least one capped diazotised compound and a coupler compound and optionally a direct dye or/and optionally an oxidizing agent free composition,
- b) then contacting the keratin fibers with an oxidizing agent or an oxidizing agent containing composition,
- c) then adjusting the pH in the range of 5 to 2 by treatment with acid, optionally in the presence of a further dye.
- d)

The present invention also concerns a process for the colouration of keratin fibers, especially human hair, with acid dyes, which can be used in combination with the method of colouring according to the present invention.

The process comprises additionally

- a) contacting the keratin fiber with an acid dye.

Customary, the dyeing composition comprising an acid dye is applied to the hair in an amount of from 50 to 100 g.

This in a composition is left on the fiber at 15 to 45°C for 1 to 30 minutes, and in particular for 0 to 15 minutes at 20 to 30°C.

Preferably the hair is rinsed and than washed with shampoo and more preferably not rinsed, but washed with shampoo.

The shampoo used herein includes a shampoo comprising 5-20% of a usual anionic surfactant such as an alkylsulfate or polyoxyethylene alkylsulfate.

Preferably the present invention relates to a method of dyeing keratin-containing fibres with the cationic reactive dyes, which comprises treating the fibres with the cationic reactive dyes defined at the beginning or with the dye compositions according to the invention.

A preferred embodiment of the method according to the invention for dyeing keratin-containing fibres comprises treating the fibres with a dyeing solution, prepared according to the process of the invention, comprising a tinctorially effective amount of a cationic reactive dye of formula (1).

The cationic reactive dyes defined at the beginning are present in the dye compositions according to the invention preferably in a tinctorially effective amount of from 0.001 % to 5 %, especially from 0.01 % to 1 %, based on the total dyestuff.

The keratin-containing fibres are usually treated with the dyeing solution for about 30 minutes at 20-25°C.

A further preferred embodiment of the present invention relates to a method of dyeing hair, which comprises treating the hair with

- a) an acidic or alkaline permanent-wave solution, and
- b) then with a composition, preferably a dyeing solution, prepared according to the process of the invention, comprising a cationic reactive dye of formula (1).

Usually the keratin-containing fibres are treated with the permanent-wave solution for about 3-10 minutes, preferably for 4-6 minutes, at 20-25°C.

A preferred embodiment of the present invention relates to a method of dyeing hair, which comprises treating the hair with a mixture of

- a) an acidic or alkaline permanent-wave solution comprising a thiol derivative, and
- b) a composition, preferably a dyeing solution comprising a cationic dichlorotriazine reactive dye or a cationic monofluoromonochloropyrimidine reactive dye.

It is generally advisable to rinse the hair after treatment with the dyeing solution and/or permanent-wave solution.

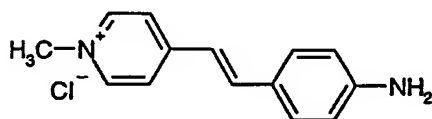
The present invention relates also to the use of the cationic reactive dyes defined at the beginning or of the dye compositions according to the invention for dyeing keratin, wool, leather, silk, cellulose or polyamides, especially for dyeing hair.

The fastness to washing properties of hair dyed in accordance with the methods of the invention using the cationic reactive dyes according to the invention are better than those of conventional permanent oxidation dyes.

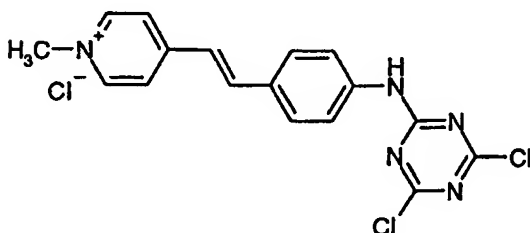
The following Examples illustrate the invention:

Example 1:

A solution containing 100 g of water and 6.5 g of a cationic chromophore of the formula below



is cooled to 0°C and adjusted to pH 4.0 by the addition of hydrochloric acid. 3.7 g of trichlorotriazine are then added at 0°C whilst maintaining the pH at pH 4 by the simultaneous dropwise addition of 10 % (% by weight) sodium carbonate solution. When the addition is complete, the pH of the resulting reaction solution is adjusted to pH 6 by the addition of further 10 % sodium carbonate solution. A suspension comprising the dye of the formula below

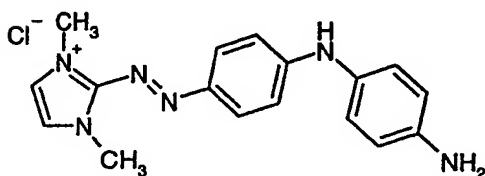


is obtained.

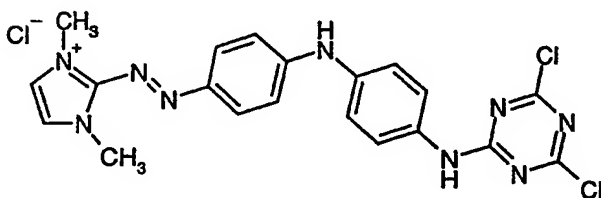
The resulting dyeing solution can be used to dye hair directly or after dilution or concentration or after isolation, optionally with the use of further additives. Hair dyed using that dyeing solution has a brilliant yellow shade and excellent fastness to washing.

Example 2:

Example 2 corresponds to Example 1, except that the cationic chromophore is replaced by that of the formula given below:



A corresponding dyeing solution comprising the cationic reactive dye of the formula below:

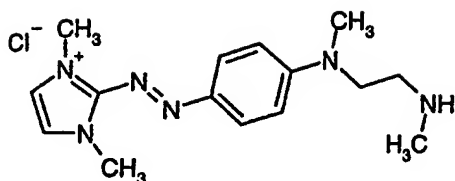


is obtained.

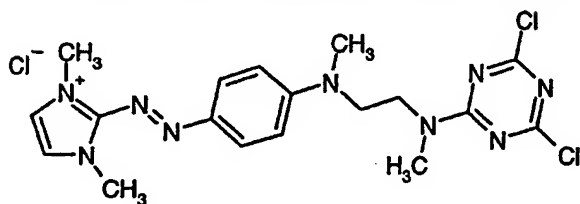
The resulting dyeing solution can be used to dye hair directly or after dilution or concentration or after isolation, optionally with the use of further additives. Hair dyed using that dyeing solution has a brilliant violet shade and excellent fastness to washing.

Example 3:

Example 3 corresponds to Example 1, except that the cationic chromophore is replaced by that of the formula below:



A corresponding dyeing solution comprising the cationic reactive dye of the formula below:

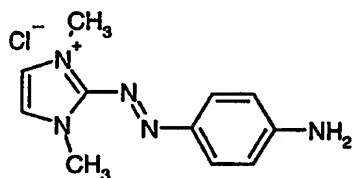


is obtained.

The resulting dyeing solution can be used to dye hair directly or after dilution or concentration or after isolation, optionally with the use of further additives. Hair dyed using that dyeing solution has a brilliant red shade and excellent fastness to washing.

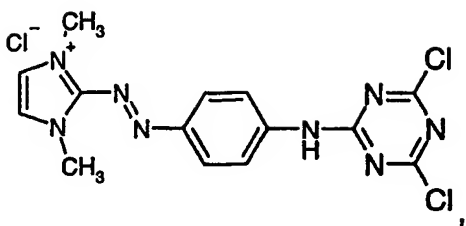
#### Example 4:

A solution of 15.9 g of a cationic chromophore of formula



in 100 g of water is added dropwise, at pH 4.0 and at a temperature in the range from 0 to 5°C, in the course of 30 minutes, to a suspension of 11.6 g of trichlorotriazine in 600 g of water. A pH of 4 is maintained by the simultaneous dropwise addition of a 1M sodium carbonate solution. After the dropwise addition, stirring is carried out for 16 hours at 0-5°C and pH 4.0. The pH of the resulting reaction suspension is then adjusted to pH 7 by the addition of further 1M sodium carbonate solution.

An orange-yellow suspension comprising the dye of the formula below



is obtained, which can be used as a dyeing solution.

The resulting dyeing solution can be used to dye hair directly or after isolation. Hair dyed using that dyeing solution has a brilliant orange-yellow shade and excellent fastness to washing.

### Application of the dyeing solutions obtained in Examples 1, 2, 3 and 4.

### Example 5:

- a) The dyeing solution obtained in Example 1, 2, 3 or 4 is applied to the hair and is left to act at room temperature for 30 minutes, and the hair is then rinsed thoroughly.
- b) Hair is pretreated with a conventional acidic or alkaline permanent-wave solution for 5 minutes at room temperature. The pretreated hair is then dyed, as under Example 5a), using a dyeing solution prepared according to Example 1, 2, 3 or 4.
- c) A dyeing solution, prepared according to any one of Examples 1, 2, 3 and 4, is mixed with a conventional permanent-wave solution. That mixture is applied to the hair and is left to act for 30 minutes at room temperature. After the action period, the hair is rinsed.

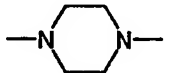
What is claimed is:

## 1. A cationic reactive dye of the general formula



wherein

A is the radical of a cationic chromophore selected from the group of the acridine, anthraquinone, azine, azo, azomethine, benzimidazole, cyanine, diazo, dioxazine, ketoimine, methine, monoazo, nitro, oxazine, polymethine, quinoline, thiazole, triarylmethane and xanthene series,

D is  $-NR-$ ,  $-(NR'-(C_1-C_7\text{alkylene})-NR'')$  or a piperazinylene of formula ,

wherein

R is hydrogen,  $C_1-C_4$ alkyl,  $-CO-C_1-C_4$ alkyl,  $-CO$ -phenyl, ortho-, meta- or para- $(C_6H_4)-(C_1-C_4$ alkyl), ortho-, meta- or para- $(C_6H_4)-(C_1-C_4$ alkylene)- $^+N(R_7R_8R_9)$ , or  $-(C_1-C_4$ alkyl)- $^+N(R_7R_8R_9)$ ,

wherein

$R_7$ ,  $R_8$  and  $R_9$  are each independently of the others hydrogen or  $C_1-C_4$ alkyl, and

$R'$  and  $R''$  are each independently of the other hydrogen or  $C_1-C_4$ alkyl, and

m is an integer 0 or 1, and

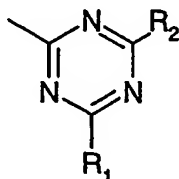
x is an integer from 1 to 8, and

$n^+$  is the charge of the radical  $[A-(D_m-B)_x]$  and is an integer from +1 to +6,

$n^-$  is the charge of the anion and is an integer from -1 to -6,

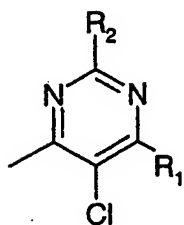
An is an anion, and

B is a fibre-reactive group of formula (2a), (2b) (2c), (2d), (2e), (2f) or (2g),

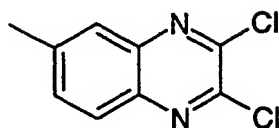


(2a),

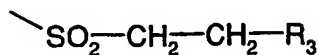




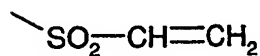
(2b) or



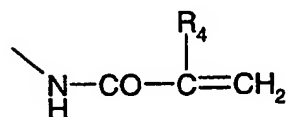
(2c)



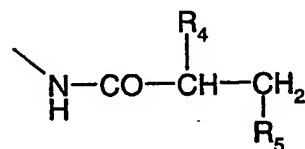
(2d),



(2e),



(2f) or

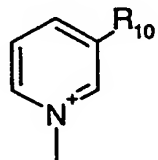


(2g),

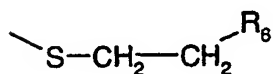
wherein

 $R_3$  is  $-\text{OSO}_3\text{X}$ ,  $-\text{OSO}_3^-$  or  $-\text{Cl}$ , $R_4$  and  $R_5$  are each independently of the other  $-\text{Cl}$  or  $-\text{Br}$ , and $R_1$  and  $R_2$  are each independently of the other  $-\text{Cl}$ ,  $-\text{F}$ ,

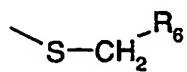
or the radical of a compound of formula (3a), (3b), (3c), (3d), (3e), (3f) or (3g),



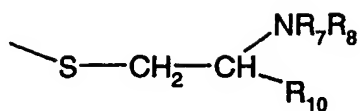
(3a),



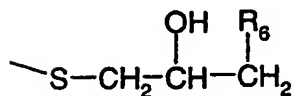
(3b),



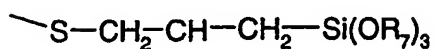
(3c),



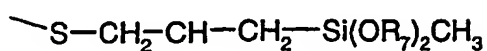
(3d),



(3e),



(3f) or



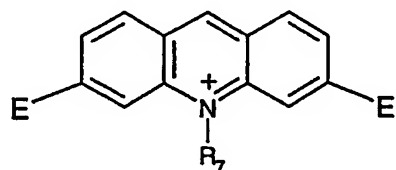
(3g),

wherein

 $\text{R}_6$  is  $\text{SO}_3^-$ ,  $\text{SO}_3\text{X}$ ,  $\text{O}^-$ ,  $\text{OX}$ ,  $\text{COO}^-$ ,  $\text{COOX}$  or  $^+\text{N(R}_7\text{ R}_8\text{ R}_9)\text{An}^-$ , $\text{X}$  is hydrogen or a cation of an alkali metal or alkaline earth metal, $\text{R}_7$ ,  $\text{R}_8$  and  $\text{R}_9$  are each independently of the others hydrogen or  $\text{C}_1\text{--C}_4$ alkyl, $\text{An}^-$  is an anion, and $\text{R}_{10}$  is  $\text{COO}^-$  or  $\text{COOX}$ ,wherein, when  $x > 1$  is, B denotes identical or not identical fibre-reactive groups.

2. A cationic reactive dye according to claim 1 of formula

a) acridine of formula

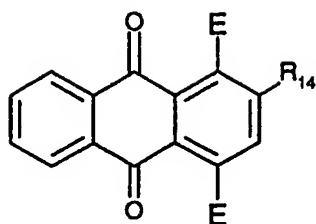
 $\text{An}^{n-}$ 

(4a),

wherein

 $\text{R}_7$ ,  $\text{An}$  and  $n^-$  are as defined above in claim 1;

b) anthraquinone of formula

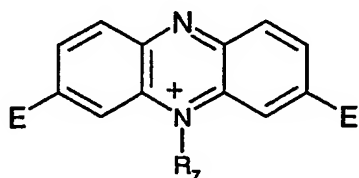


(4b),

wherein

$R_{14}$  is  $-S-(C_1-C_4)-^+NR_7R_8R_9 An^{n-}$ , preferably  $-S-(ethylene)-^+N(CH_3)_3 An^{n-}$ , and  $An$ ,  $R_7$ ,  $R_8$ ,  $R_9$  and  $n^-$  are as defined above in claim 1;

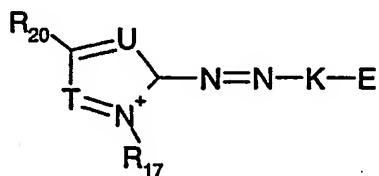
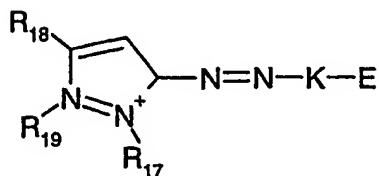
c) azine of formula

 $An^{n-}$  (4c),

wherein

$R_7$ ,  $n^-$  and  $An$  are as defined above in claim 1;

d) azo compound of formula

 $An^{n-}$  (4d) or $An^{n-}$  (4e),

wherein

$U$  is  $-O-$ ,  $-S-$  or  $-NR_{17}-$ ,

$T$  is  $-CH=$ ,  $-CR_{17}=$  or  $-N=$ ,

$R_{17}$  and  $R_{19}$  are each independently of the other  $C_1-C_4$ alkyl unsubstituted or substituted by  $OH$ ,  $C_1-C_4$ alkoxy, halogen,  $CN$ , amino,  $C_1-C_4$ monoalkylamino or by di- $C_1-C_4$ alkylamino,

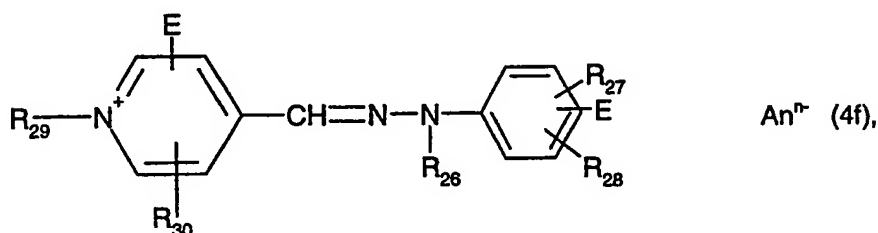
$R_{18}$  is hydrogen,  $C_1$ - $C_4$ alkyl, chlorine or nitro,

$R_{20}$  is hydrogen,  $C_1$ - $C_4$ alkyl, chlorine, nitro, amino,  $C_1$ - $C_4$ monoalkylamino or di- $C_1$ - $C_4$ alkyl-amino,

K is the radical of a coupling component from the aniline or phenol series or the radical of a heterocyclic coupling component, and

$n^-$  and An are as defined in claim 1;

d) azomethine of formula



wherein

$R_{30}$  is hydrogen,  $C_1$ - $C_4$ alkyl or CN,

$R_{29}$  is  $C_1$ - $C_4$ alkyl unsubstituted or substituted by OH or by CN,

$R_{28}$  is hydrogen or  $C_1$ - $C_4$ alkyl,

$R_{27}$  and  $R_{28}$  are each independently of the other hydrogen,  $C_1$ - $C_4$ alkyl or  $C_1$ - $C_4$ alkoxy, or

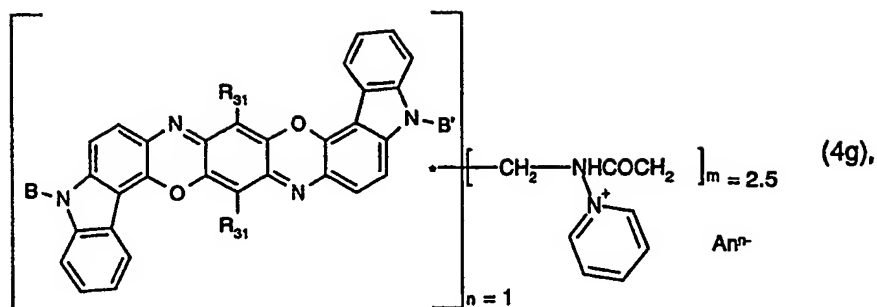
$R_{27}$  is fluorine in the ortho position, with  $R_{30}$  and  $R_{28}$  being hydrogen and  $R_{29}$  and  $R_{28}$  being methyl, or

$R_{27}$  is chlorine in the para position, with  $R_{30}$  and  $R_{28}$  being hydrogen and  $R_{29}$  and  $R_{28}$  being methyl, or

$R_{26}$  and  $R_{27}$  together with the nitrogen and carbon atoms bonding them form a 5- or 6-membered ring, and

$n^-$  and An are as defined above in claim 1;

e) dioxazine of formula



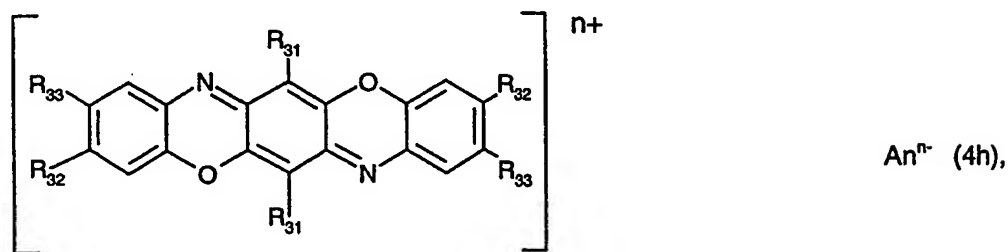
wherein

B' is B or hydrogen, and

R<sub>31</sub> is hydrogen, halogen, C<sub>1</sub>-C<sub>24</sub>alkyl or E,

n<sup>-</sup> and An are as defined above in claim 1;

or dioxazine of formula

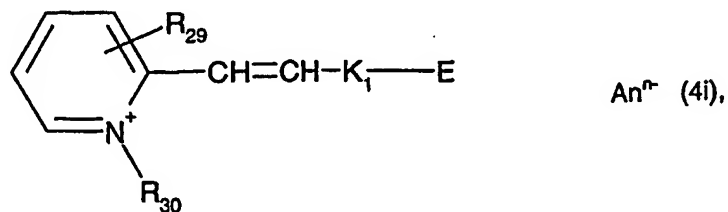


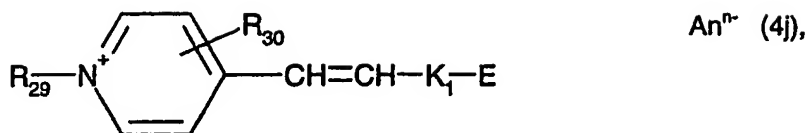
wherein

R<sub>31</sub>, R<sub>32</sub> and R<sub>33</sub> are each independently of the others hydrogen, halogen, C<sub>1</sub>-C<sub>4</sub>alkyl, C<sub>1</sub>-C<sub>4</sub>-alkoxy or E, and

n<sup>-</sup> and An are as defined above in claim 1;

f) methine of formula



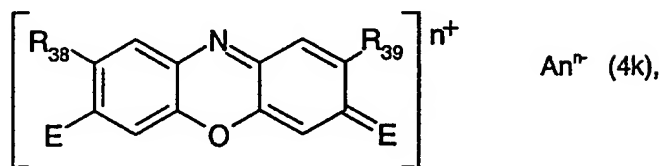


wherein

$\text{R}_{29}$ ,  $\text{R}_{30}$ ,  $n^-$  and An are as defined above and

$\text{K}_1$  is the radical of an aromatic or heterocyclic amine;

g) oxazine of formula



wherein

$\text{R}_{38}$  and  $\text{R}_{39}$  are each independently of the other E,  $\text{C}_1\text{-C}_4$ alkyl or  $\text{C}_1\text{-C}_4$ alkoxy, and

$n^-$ ,  $n^+$  and An are as defined above in claim 1;

and, in the above-mentioned formulae, E is in each case ( $\text{D}_m\text{-E}'$ ), wherein

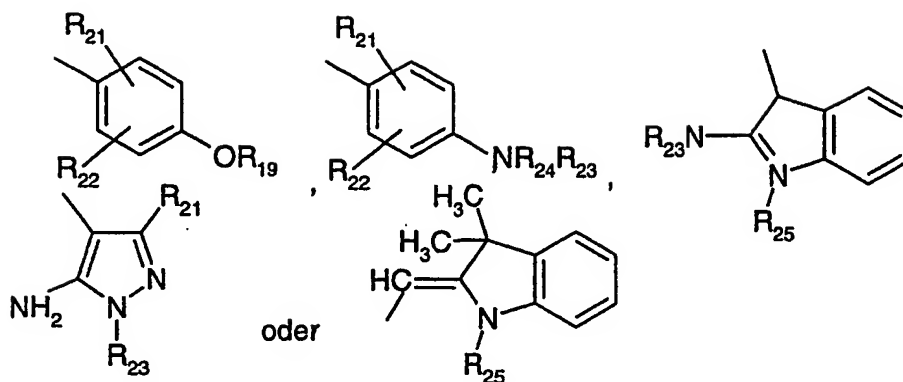
D and m are as defined above in claim 1, and

$\text{E}'$  is hydrogen or B,

with the proviso that E in each formula is at least once ( $\text{D}_m\text{-E}'$ ) wherein

$\text{E}'$  is B, and B is as defined above in claim 1.

3. A cationic reactive dye according to claim 2 of formula (4d) or (4e) wherein the radicals – K-E together form a compound of the formulae given below



wherein

$R_{19}$  is hydrogen or B, or  $C_1$ - $C_4$ alkyl unsubstituted or substituted by E, OH,  $C_1$ - $C_4$ alkoxy, halogen, CN, amino,  $C_1$ - $C_4$ monoalkylamino or by di- $C_1$ - $C_4$ alkylamino,

$R_{21}$  and  $R_{22}$  are each independently of the other E, OH,  $C_1$ - $C_4$ alkoxy, halogen, CN, amino,  $C_1$ - $C_4$ monoalkylamino or by di- $C_1$ - $C_4$ alkylamino, or  $C_1$ - $C_4$ alkyl unsubstituted or substituted by E, OH,  $C_1$ - $C_4$ alkoxy, halogen, CN, amino,  $C_1$ - $C_4$ monoalkylamino or by di- $C_1$ - $C_4$ alkylamino,

$R_{23}$  and  $R_{24}$  are each independently of the other hydrogen or B, or  $C_1$ - $C_4$ alkyl unsubstituted or substituted by OH,  $C_1$ - $C_4$ alkoxy, halogen, CN, amino,  $C_1$ - $C_4$ monoalkylamino or by di- $C_1$ - $C_4$ alkylamino, or

$R_{23}$  and  $R_{24}$  together with the nitrogen atom bonding them form a 5- or 6-membered ring unsubstituted or substituted by E, or

$R_{21}$  and  $R_{23}$  together with the nitrogen and carbon atoms bonding them form a 5- or 6-membered ring unsubstituted or substituted by E, or

$R_{22}$  and  $R_{24}$  together with the nitrogen and carbon atoms bonding them form a 5- or 6-membered ring unsubstituted or substituted by E, and

$R_{25}$  is hydrogen or B, or  $C_1$ - $C_4$ alkyl unsubstituted or substituted by E, OH,  $C_1$ - $C_4$ alkoxy, halogen, CN, amino,  $C_1$ - $C_4$ monoalkylamino or by di- $C_1$ - $C_4$ alkylamino, and

E is in each case ( $D_m$ -E'), wherein

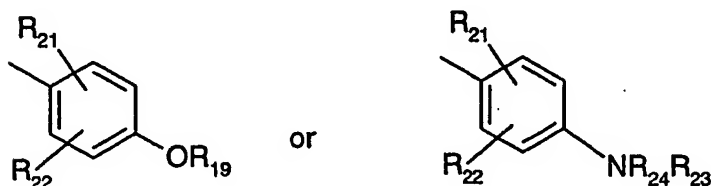
D and m are as defined in claim 1, and

E' is hydrogen or B,

with the proviso that E in each formula is at least once ( $D_m$ -E') wherein

E' is B, and B has the definitions or preferences given in claim 1.

4. A cationic reactive dye according to either claim 2 or claim 3 of formula (4d) or (4e), wherein the radicals -K-E denote a compound of the formulae given below



wherein

$R_{19}$  is hydrogen or B, or unsubstituted  $C_1$ - $C_4$ alkyl,

$R_{21}$  and  $R_{22}$  are each independently of the other hydrogen, E, unsubstituted  $C_1$ - $C_4$ alkyl,  $C_1$ - $C_4$ alkoxy or halogen,

$R_{23}$  and  $R_{24}$  are each independently of the other hydrogen or B, or unsubstituted  $C_1$ - $C_4$ alkyl, or

$R_{23}$  and  $R_{24}$  together with the nitrogen atom bonding them form a pyrrolidine, piperidine, morpholine or piperazine ring unsubstituted or substituted by E, or

$R_{21}$  and  $R_{23}$  together with the nitrogen atom and carbon atom bonding them form a pyrrolidine, piperidine, morpholine or piperazine ring unsubstituted or substituted by E, or

$R_{22}$  and  $R_{24}$  together with the nitrogen atom and carbon atom bonding them form a pyrrolidine, piperidine, morpholine or piperazine ring unsubstituted or substituted by E; and

E is in each case ( $D_m$ -E'), wherein

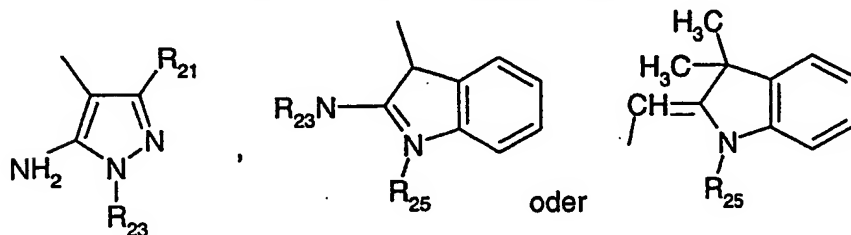
D and m are as defined in claim 1, and

E' is hydrogen or B,

with the proviso that E in each formula is at least once ( $D_m$ -E') wherein

E' is B, and B has the definitions or preferences given in claim 1.

5. A cationic reactive dye according to claim 2 of formula (4i) or (4j), wherein the radicals -K<sub>1</sub>-E denote a compound of the formulae given below





wherein

$R_{21}$  is E,  $C_1$ - $C_4$ alkyl,  $C_1$ - $C_4$ alkoxy or halogen,

$R_{23}$  and  $R_{25}$  are each independently of the other hydrogen or B, or  $C_1$ - $C_4$ alkyl unsubstituted or substituted by OH,  $C_1$ - $C_4$ alkoxy, halogen, CN, amino,  $C_1$ - $C_4$ monoalkylamino or by di- $C_1$ - $C_4$ alkylamino, and

E is in each case ( $D_m$ -E'), wherein

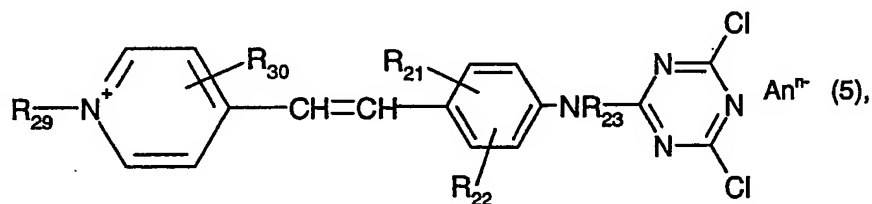
D and m are as defined in claim 1, and

E' is hydrogen or B,

with the proviso that E in each formula is at least once ( $D_m$ -E') wherein

E' is B, and B has the definitions or preferences given in claim 1.

6. A cationic reactive dye according to claim 2 of formula



wherein

$R_{21}$  and  $R_{22}$  are each independently of the other hydrogen,  $C_1$ - $C_4$ alkyl,  $C_1$ - $C_4$ alkoxy or halogen,

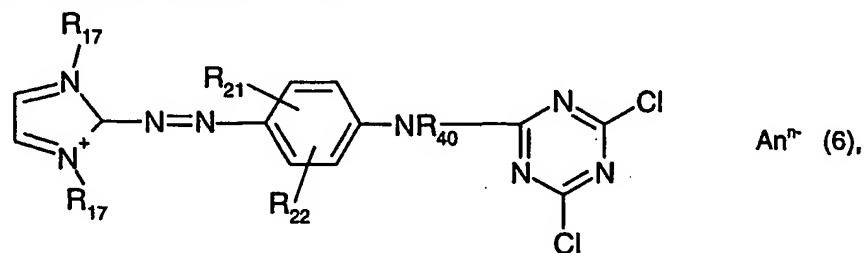
$R_{23}$  is hydrogen or unsubstituted  $C_1$ - $C_4$ alkyl,

$R_{29}$  is  $C_1$ - $C_4$ alkyl unsubstituted or substituted by OH or by CN, and

$R_{30}$  is hydrogen,  $C_1$ - $C_4$ alkyl or CN, and

An and  $n^-$  are as defined above in claim 1,

or a cationic reactive dye of formula

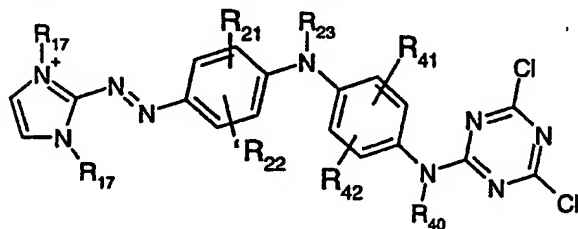


wherein

$R_{17}$  and  $R_{40}$  are each independently of the other hydrogen, or  $C_1$ - $C_4$ alkyl unsubstituted or substituted by OH,  $C_1$ - $C_4$ alkoxy, halogen, CN, amino,  $C_1$ - $C_4$ monoalkylamino or by di- $C_1$ - $C_4$ -alkylamino, and

An and  $n^+$ ,  $R_{21}$  and  $R_{22}$  are as defined above,

or a cationic reactive dye of formula



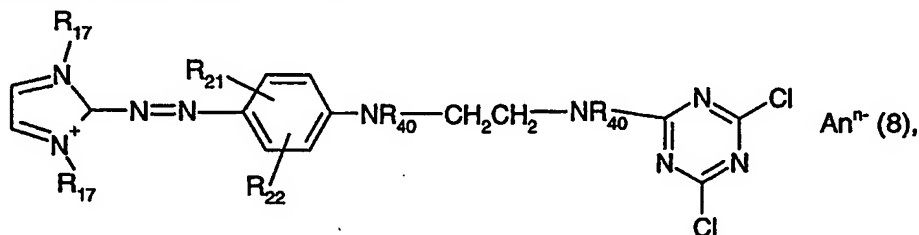
An<sup>n+</sup> (7)

wherein

An,  $n^+$ ,  $R_{17}$ ,  $R_{40}$ ,  $R_{21}$ ,  $R_{22}$  and  $R_{23}$  are as defined above, and

$R_{40}$  and  $R_{41}$  are each independently of the other hydrogen, or  $C_1$ - $C_4$ alkyl unsubstituted or substituted by OH,  $C_1$ - $C_4$ alkoxy, halogen, CN, amino,  $C_1$ - $C_4$ monoalkylamino or by di- $C_1$ - $C_4$ -alkylamino,

or a cationic reactive dye of formula



An<sup>n+</sup> (8),

wherein  $R_{17}$ ,  $R_{21}$ ,  $R_{22}$ ,  $R_{40}$ , An and  $n^+$  are as defined above.

7. A process for the preparation of a cationic reactive dye of formula (1) according to claim 1, in which process a cationic chromophore A is reacted with x fibre-reactive groups B and where appropriate with m bridging members D, wherein A, B, D, x and m are as defined above in claim 1.

8. A dye composition comprising a cationic reactive dye according to any one of claims 1 to 6.

9. A method of dyeing keratin-containing fibres, which comprises treating the fibres with a cationic reactive dye according to any one of claims 1 to 6 or with a dye composition according to claim 8.

10. A method of dyeing hair, which comprises treating the hair with an acidic or alkaline permanent-wave solution, and  
then with a composition comprising a cationic reactive dye of formula (1) according to claim 1.

11. A method of dyeing hair, which comprises treating the hair with  
a) a mixture of an acidic or alkaline permanent-wave solution comprising a thiol derivative and  
b) a composition comprising a cationic dichlorotriazine reactive dye or a cationic monofluoromonochloropyrimidine reactive dye according to claim 1.

12. Use of a cationic reactive dye according to any one of claims 1 to 6 or of a dye composition according to claim 8 for dyeing keratin, wool, leather, silk, cellulose or polyamides.

13. Use of a cationic reactive dye according to any one of claims 1 to 6 or of a dye composition according to claim 8 for dyeing hair.

# INTERNATIONAL SEARCH REPORT

Intern. Application No  
PCT/EP 02/10404

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C09B62/04 C09B62/085 C09B44/16 A61K7/13

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C09B A61Q A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 34 24 320 A (SANDOZ AG) 23 January 1986 (1986-01-23) examples 1,2,4-6,12-15,17,40,44,47,54 claims; examples 55,59,60,64,67,70,73-79,A-D	1,8,12
X	US 3 338 660 A (WALTER BIEDERMANN) 29 August 1967 (1967-08-29) examples 71,83,93,94,129,146	1,8,12
X	-& GB 1 027 570 A (J.R. GEIGY AG.) 27 April 1966 (1966-04-27) examples 16,43,47,66	1,8,12
X	US 5 175 259 A (KESSEL KNUT ET AL.) 29 December 1992 (1992-12-29) examples 20,68	1,8,12
	-/-	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

16 January 2003

Date of mailing of the international search report

28/01/2003

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# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 02/10404

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 714 954 A (CIBA GEIGY AG) 5 June 1996 (1996-06-05) cited in the application claims; example 3 -----	1-13
A	WO 95 01772 A (CIBA GEIGY AG ; MOECKLI PETER (CH)) 19 January 1995 (1995-01-19) cited in the application claims; examples -----	1-13

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 02/10404

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
DE 3424320	A	23-01-1986	DE 3424320 A1	23-01-1986
			AU 593772 B2	22-02-1990
			AU 4546885 A	10-02-1986
			CA 1248941 A1	17-01-1989
			DE 3565407 D1	10-11-1988
			WO 8600632 A1	30-01-1986
			EP 0188473 A1	30-07-1986
			ES 8608553 A1	01-12-1986
			JP 61502611 T	13-11-1986
			NZ 212589 A	29-05-1989
			US 4820806 A	11-04-1989
US 3338660	A	29-08-1967	BE 646971 A	23-10-1964
			CH 405228 A	30-09-1965
			DE 1469754 A1	09-04-1970
			FR 1391408 A	05-03-1965
			GB 1027570 A	27-04-1966
			NL 6404498 A	26-10-1964
US 5175259	A	29-12-1992	DE 4107377 A1	10-09-1992
			DE 59200247 D1	28-07-1994
			EP 0503339 A1	16-09-1992
			JP 4345669 A	01-12-1992
EP 0714954	A	05-06-1996	CA 2161947 A1	04-05-1996
			DE 59510392 D1	31-10-2002
			EP 1219683 A2	03-07-2002
			EP 0714954 A2	05-06-1996
			JP 8225538 A	03-09-1996
			US 5708151 A	13-01-1998
WO 9501772	A	19-01-1995	AU 687849 B2	05-03-1998
			AU 7344894 A	06-02-1995
			BR 9405500 A	08-09-1999
			CA 2142091 A1	19-01-1995
			CN 1111444 A ,B	08-11-1995
			DE 69428096 D1	04-10-2001
			DE 69428096 T2	02-05-2002
			WO 9501772 A1	19-01-1995
			EP 0658095 A1	21-06-1995
			ES 2161775 T3	16-12-2001
			JP 8501322 T	13-02-1996
			JP 3281386 B2	13-05-2002
			MX 9405076 A1	31-01-1995
			US 5733343 A	31-03-1998